

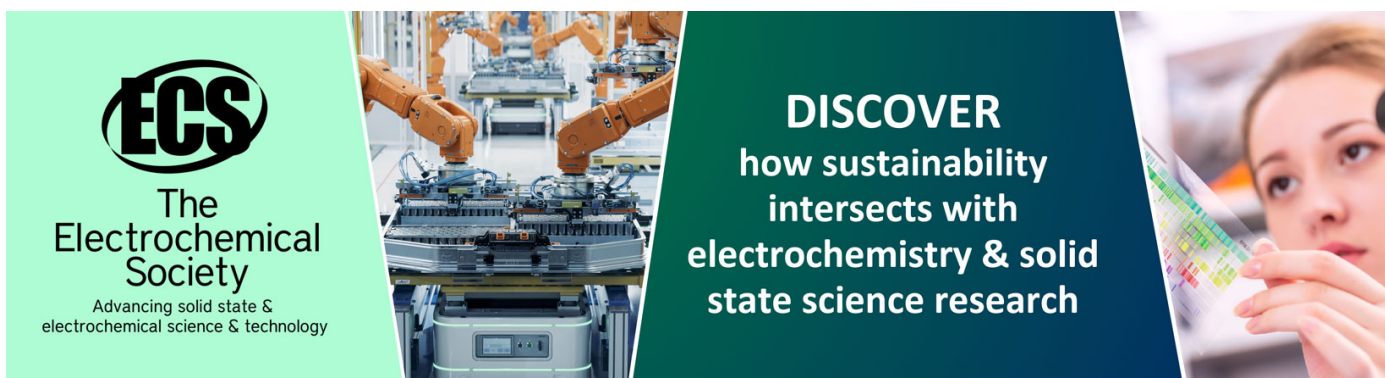
Macromolecular smart materials and structures

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Macromolecular smart materials and structures

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Abstract. Macromolecules offer many ways of creating smart materials. New capabilities for the predictive design of polymer molecules are coming from the rapid advances in computer modelling of the structure and properties of large molecules. Powerful chemical methods for the creation of polymeric modules that can be assembled in a variety of ways to perform useful, smart molecule functions are available. It has only recently become possible to observe directly segments of polymer molecules attached to solid surfaces, thanks to the techniques of scanning tunnelling microscopy and atomic force microscopy. This paper describes a combined approach, utilizing these new capabilities, to the design, synthesis and characterization of a smart macromolecule which can function to control damage at the interface between a polymer matrix and a reinforcing fibre, and can also provide a colour change which will reveal the presence of the damaged region.

1. Introduction

Smart molecules are designed to receive a stimulus, transmit or process it, and then to respond by producing a useful effect, which may include a signal showing that the smart material is working. Stimuli may include strain, stress, incident photons, small molecules, an electric field, hydrostatic pressure, or the like. Processing or transmission of the signal may include absorption of a photon, reaction with a small molecule, integration of a series of events, translation or rotation of segments of a polymer molecule, creation and motion of crystallographic defects or other localized conformations that produce reptation or twisting of segments [1], and the alteration of localized stress fields, for example. The useful effects produced may be a colour change, a change in the index of refraction tensor, a change in the stress distribution, a different connectivity of the parts of a molecule or a network, or a change in volume.

Our approach to smart materials based on polymer molecules is modular. The elementary functions of reception of a stimulus, transmission, processing, actuation, and the like are incorporated into oligomers which have reactive groups at the ends or at other strategic positions. The synthesis of such oligomers, and their attachment together, are active areas in the state-of-the-art of polymer synthetic chemistry [2–5]. The reactive groups are used to assemble the desired set of functions required for a particular smart material by bonding together the oligomers that have the desired functions. The oligomers described above usually contain only one backbone chain and may involve only a few hundred atoms.

Alternatively, the elementary functions of a smart material based on polymers may be incorporated into a larger polymer molecule, or group of molecules. A few thousand atoms may be involved. In this case, the properties of the module may be usefully described in terms of thermodynamic or bulk properties.

Contemporary computer modelling encompasses both of these size ranges [6]. The behaviour of oligomers, and systems of connected oligomers, can be calculated from knowledge of the electronic states of the molecules or from knowledge of the interatomic potential functions. Computer modelling can also predict the thermodynamic and bulk properties of the larger aggregates that may also be used to design polymeric smart material systems. To distinguish these size ranges, we use the phrase ‘molecular scale’ for the smaller and the word ‘nanophase’ for the larger.

Information about the molecular scale behaviour of smart materials is also available from the direct observation of oligomers, using the techniques [7] of atomic force microscopy and scanning tunnelling microscopy. The attachment of oligomers to a solid surface is observed directly and used to help understand the behaviour of a smart molecule system.

The work described in this paper combines computer modelling for molecular design, direct observation of polymer molecules on a surface, and state-of-the-art polymer synthesis, which provides the means for making complex linear chains or networks with segments having a wide variety of structures and functions.

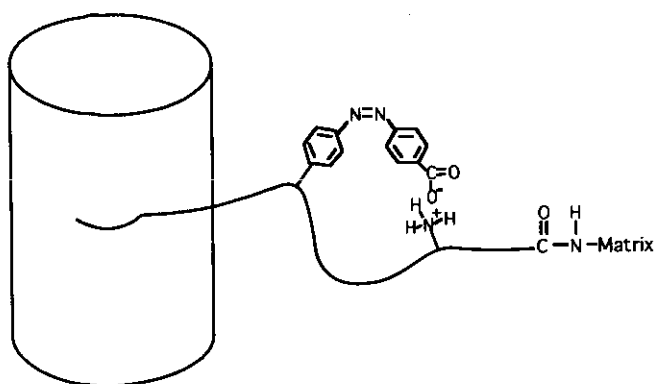


Figure 1. Diagram of a smart macromolecule at the interface between a fibre and its matrix.

2. Modules for a molecular-scale smart material system

An interesting example of a smart material system can be designed at the molecular scale to deal with the possibility that separation may occur at the polymer–matrix interface in a fibre reinforced composite when the composite is damaged by excess mechanical deformation. Figure 1 shows a schematic diagram of such a molecule and figure 2 shows an example of the molecular structure.

Such a smart molecule would have an oligomer that attaches the smart molecule to the fibre. This attachment oligomer is connected to two branches. The first branch contains a stress-sensitive chromophore and a weak link in series. The second branch contains a longer, strong chain which can carry the load when the weak link is pulled apart. The two branches are rejoined and connected to an oligomer that attaches to the polymer matrix. Figure 3 shows this smart molecule after the fibre has begun to separate from the matrix.

The modular functions that are needed are:

- (i) attachment to the fibre;

- (ii) a weak link that breaks as soon as a pre-determined amount of separation occurs;
- (iii) a piezochromic group that changes its colour when the separation occurs;
- (iv) a loose loop of polymer which maintains a useful level of attachment even after the fibre and the matrix have separated by an anticipated amount;
- (v) attachment to the matrix.

This smart material system receives and detects a signal from the strain field that separation at the interface is occurring as the point of attachment to the matrix moves away from the point of attachment to the fibre. The colour change provides a signal that the separation has produced significant damage. The loose loop acts as a molecular ‘keeper chain’ that tends to prevent the interfacial separation from growing to a catastrophic failure of the composite part. Such a smart material system is helpful in composite systems in which impact damage, which produces little visible change, can leave the composite unable to bear the expected compressive loads. This smart molecule would reside and function in whatever interphase [8, 9] region is present.

Figure 4 shows a diagram of a variation of this smart molecule in which separation at the weak link increases the freedom for conformational changes at the chromophore by separating one or more hydrogen bonds in the oligomer. The hydrogen bonds serve as latches to hold the chromophore in a desired conformation until the molecule is stretched as shown in figure 5.

3. Oligomeric module for attachment to the fibre

The attachment of an oligomeric module to graphite was studied. The oligomer chosen for study is octadecyl amine, which might attach to reactive sites on the graphite through the amine group, or alternatively, through the Van der Waals attraction of the hydrogen

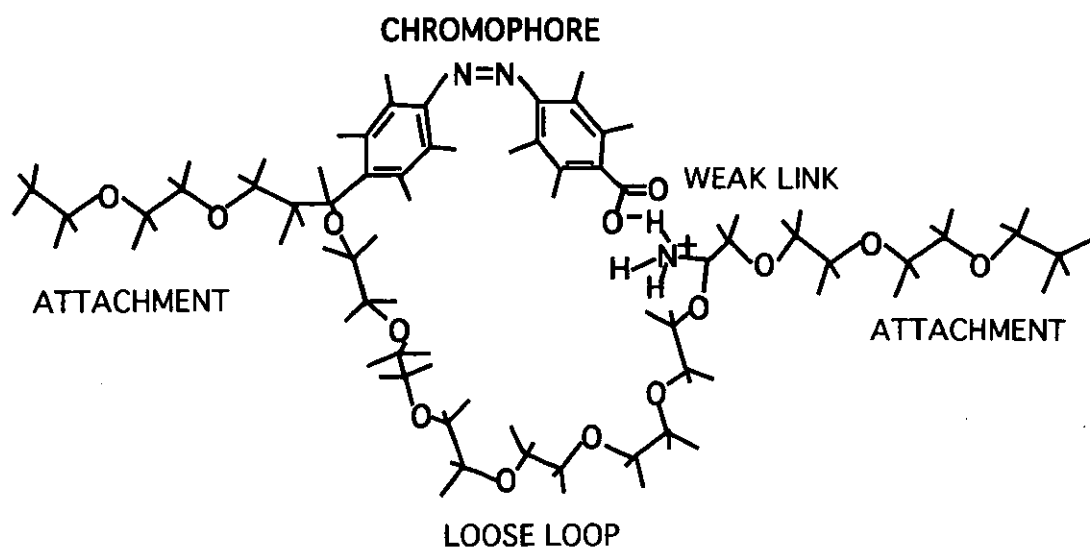


Figure 2. A molecular-scale design for the smart macromolecule.

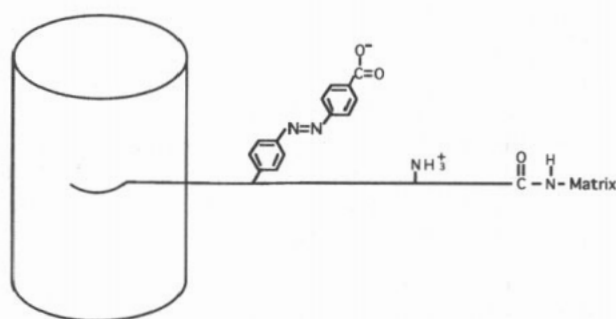


Figure 3. Diagram of the smart macromolecule after the fibre has begun to separate from the matrix.

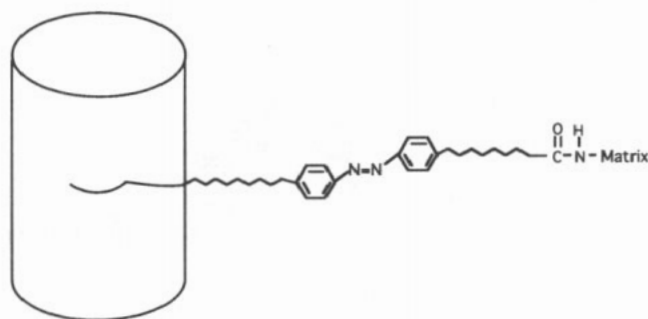


Figure 5. The smart macromolecule shown in figure 4 after the beginning of separation of the fibre from the polymer matrix.

atoms to the graphite surface. Graphite was chosen because it is similar to the carbon or graphite fibres used in composites, and to the carbon black used in the manufacture of rubber. Graphite surfaces with monatomic steps were prepared by cleavage of highly orientated pyrolytic graphite. In some samples the cleavage surface was chemically oxidized to create steps that were one, or several, atomic layers high.

The objective of this work is primarily to demonstrate the modular approach to show how smart macromolecules can be designed and perhaps used. We recognize that a colour change at the interface of a graphite fibre will be of limited usefulness. However, a very similar approach can be used for the design and characterization of smart molecules for the interface of glass or other transparent fibres if atomic force microscopy is substituted for the scanning tunnelling microscopy, which works so well on graphite crystals.

The attachment to graphite, of individual oligomers such as octadecyl amine, was directly observed with the scanning tunnelling microscope and the atomic force microscope (see figures 6 and 7). The octadecyl amine molecules tend to lie flat on the graphite, with the molecule in a planar zigzag conformation.

4. The weak link module

Various kinds of weak links may be useful. Any bond that will separate before the tensile force along the chain causes a primary backbone bond to separate can be considered to be a weak link. An ionic bond, such as that between an amide and a carboxyl is expected to break before the covalent bonds in the chain. This type of break, in the molecule shown in figure 1, would completely sever one of the two branches and leave the chromophore attached to a side branch with one of its ends not constrained.

Hydrogen bonds are much weaker bonds, so the first effect of tension in the oligomer in figure 4 is to break these bonds. Once the hydrogen bonds are broken, the region of the molecule containing the chromophore has more freedom to undergo the conformational changes associated with a change in its colour.

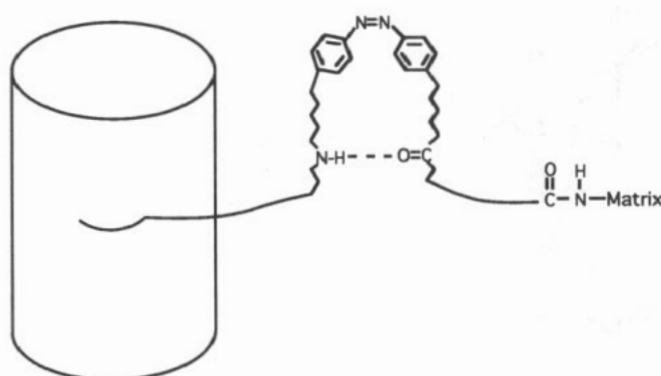


Figure 4. A smart macromolecule in which the conformation of the chromophore is stabilized by a hydrogen bond.

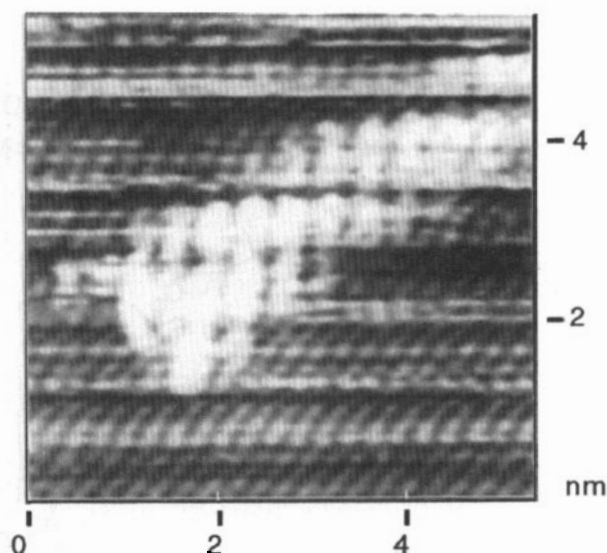


Figure 6. Scanning tunnelling micrograph of octadecyl amine physically absorbed on the cleavage plane of graphite. Partly resolved carbon atoms surround the row of absorbed molecules.

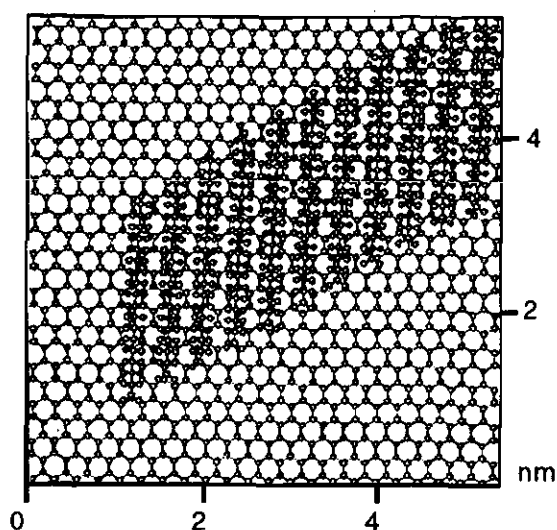


Figure 7. Computer generated drawing of octadecyl amine on graphite, showing how the scanning tunnelling micrograph is interpreted.

5. The piezochromic module

Both azo compounds and stilbenes are chromophores that are known to undergo colour changes when they are transformed between the cis and the trans forms [10, 11]. Since the trans form is longer than the cis form, a tensile force applied to the cis form can be expected to increase the probability that it will change to the trans form. For some molecules, which are stable in the cis form, and for which the change to the trans form provides the desired colour change, the problem is simply to incorporate the molecule into a diblock copolymer in such a way that the expected strains in the material will be transmitted to the molecule as a tensile force.

Elastomers and plastics with stress-sensitive chromophores in the polymer backbone was synthesized. Using the methodology of living anionic polymerization, polymers can be prepared which have controlled molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, tacticity, and branching. Because these are living polymerizations, the product is a polymeric carbanion which can be reacted with a variety of electrophiles to form end-functionalized polymers.

Omega-carboxyl-terminated polystyrene and omega-carboxyl-terminated poly(styrene-block-butadiene) polymers were prepared as shown in Scheme 1 of figure 8. These chain-end functionalized polymers were converted to the corresponding acid chlorides and then reacted with azodianiline to introduce the azo linkage into the polymer and couple the two chains together as shown in Scheme 2 of figure 8.

These polymers are being characterized with respect to their structure. The effect of irradiation and stress on their ultra-violet-visible absorption spectra is being measured. In order to increase the concentration of chromophores in the samples, alpha,omega-difunctional elastomers are being prepared which will form segmented

block copolymers upon reaction with difunctional chromophores such as azodianiline.

There is a class of azo and stilbene molecules for which the most stable form is the trans form. For these molecules to respond to a tensile force with a colour change, the molecule must be held in the cis form by a latch that can be opened by a tensile force in the molecule. Figure 9 shows the molecular detail of such a 'latch' which was shown diagrammatically in figure 4. The conformation shown is chosen to reveal the structure of the molecule. The molecule is presumed to lie at an interface, shown by a vertical broken line, between polystyrene on the left and polybutadiene on the right.

The azo or stilbene molecule is held in the cis form by hydrogen bonds on short oligomers attached to either end of the chromophore. The polymer chains represented by the circles serve as attachments to the polymer on either side of the interface. If the circles are interpreted as spheres filled with polymer, and drawn on the same scale as the molecule, the polybutadiene sphere would have a molecular weight of about 1700 g mol^{-1} and the polystyrene sphere would have a molecular weight of about 2800 g mol^{-1} . This corresponds to 31 repeat units of polybutadiene and 28 repeat units of polystyrene.

A tensile force in the longer chain first pulls the hydrogen bonds apart, and this allows the chromophore to change to the trans conformation and produces the desired colour change. The main chain remains intact and transfers force across the interface. Phase separated blends offer a way of testing the behaviour of smart molecules in the high strain field which can be generated near the interface of a hard and a soft phase.

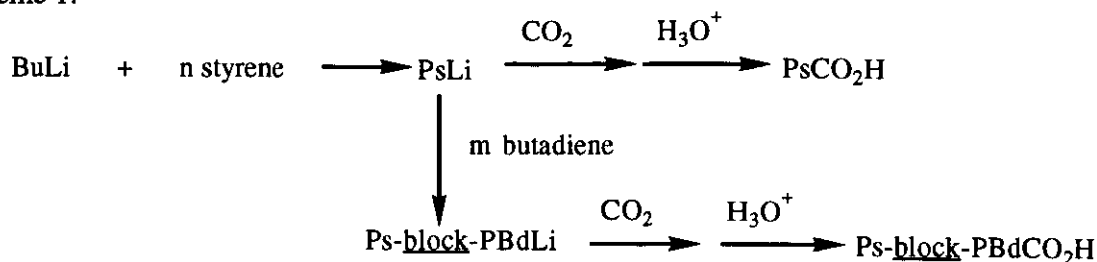
The lower part of figure 9 shows schematically how the shape of the molecule might change for a strain of about 200%. Strains of this magnitude might occur within one or two nanometres of a broken or unbonded fibre. The behaviour of each of the polymer blocks is based on the tensile modulus of bulk polystyrene and polybutadiene, respectively.

For the part of the molecule shown in detail in figure 9, which contains an azo chromophore held in the cis conformation by hydrogen bond latches, the relation between energy and strain was calculated in the following way. The ends of the segment were constrained at a succession of points of increasing separation distance in the stress direction indicated in figure 10.

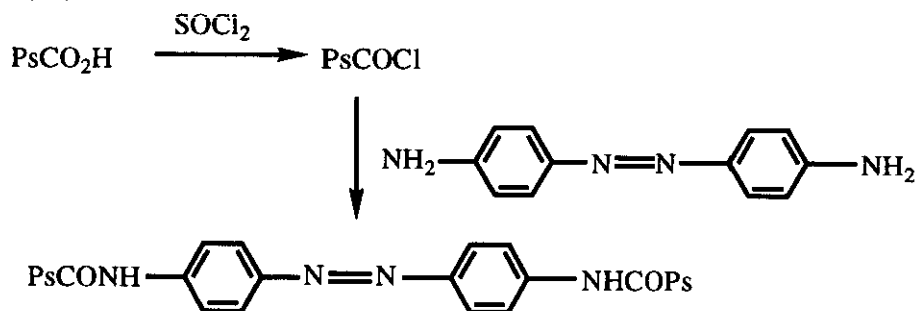
A minimum energy conformation of the segment was calculated for each distance. The value of the minimum energy was plotted as a function of the distance. The initial distance between the ends was about 1.95 nm, and this was used to calculate the strain for each separation distance.

Figure 10 shows the energy of such a molecule on the basis of the interatomic potentials calculated as a function of the increase in separation of the ends and the corresponding strain. The energy was calculated with SYBYL molecular modelling software [12]. Molecular dynamics calculations, which would deal with the thermal mobility of chain segments, are quite practical on molecules of this size, and would probably result in a more realistic curve.

Scheme 1.



Scheme 2.

**Figure 8.** Two schemes for the preparation of polymers containing stress sensitive chromophores.

Also, refined estimates of the stress associated with the light-induced change in the conformation of azobenzene from *trans* to *cis* are being obtained. The molecules being considered are an azobenzene with different kinds of polymer chains appended in the para positions of each benzene ring. One approach utilizes a variation of the method described by Flory [13] for the computation of the average of the end-to-end vectors of the attached polymer chains. The magnitude of the stresses induced by photo-isomerization are expected to be proportional to the differences in the end-to-end distances of the polymers caused by the *trans* to *cis* isomerization.

For a chromophore to change its conformation, or for a weak bond to separate, the energy from the strain field concentrated in that particular oligomer must be at least large enough to overcome the potential barriers of the sort shown in figure 10. Thermally excited vibrations can provide some of the energy, but for the molecule to perform as intended, the thermal energy should not cause transitions in the absence of strain.

A useful starting point for predicting the response of such a molecule to a tensile force is to choose an effective spring constant that will store an energy which is equivalent to the maximum energy of the barrier when the spring is stretched to the strain at which the maximum occurs. The parabola in figure 10 shows the elastic energy in a linear spring that has a force constant which makes the energy in the spring equal to the calculated energy increase in the molecule at the strain at which the highest barrier occurs. This approximation, combined with the use of the bulk modulus for the polymer attachments to the bulk phases, is the basis for the diagram shown in

figure 9. In fact, this analysis suggests that the polybutadiene ellipse should be somewhat more elongated for the conditions shown. If each functional oligomer is approximated as a linear spring, then it is easy to calculate the strain and the elastically stored energy in each oligomer. It remains, however, something of an art to choose an appropriate spring constant that will represent the essential features of the rather complicated curve of figure 10.

6. The loose loop module

The loose loop is a linear polymer with functional groups chosen to permit assembly into the smart molecule. Its length and morphology are variables that affect its performance in the smart material. The length should be such that the expected displacement of the fibre and the matrix can be spanned. On the other hand, if the loose loop is longer than the anticipated displacement, the loop may not carry as much of the force as it should. Further, the material in the extra length may occupy space that is needed for the primary attachments between the fibre and the matrix.

A randomly coiled molecule could be extended but self-entanglements are likely to be a problem that is particularly difficult to resolve at low temperatures. A chain crystallized in the folded chain morphology could be extended with a smaller probability of becoming entangled with itself or its neighbours. An idealized morphology would be a molecular helix analogous to the helical cable often used to attach the handset of a telephone.

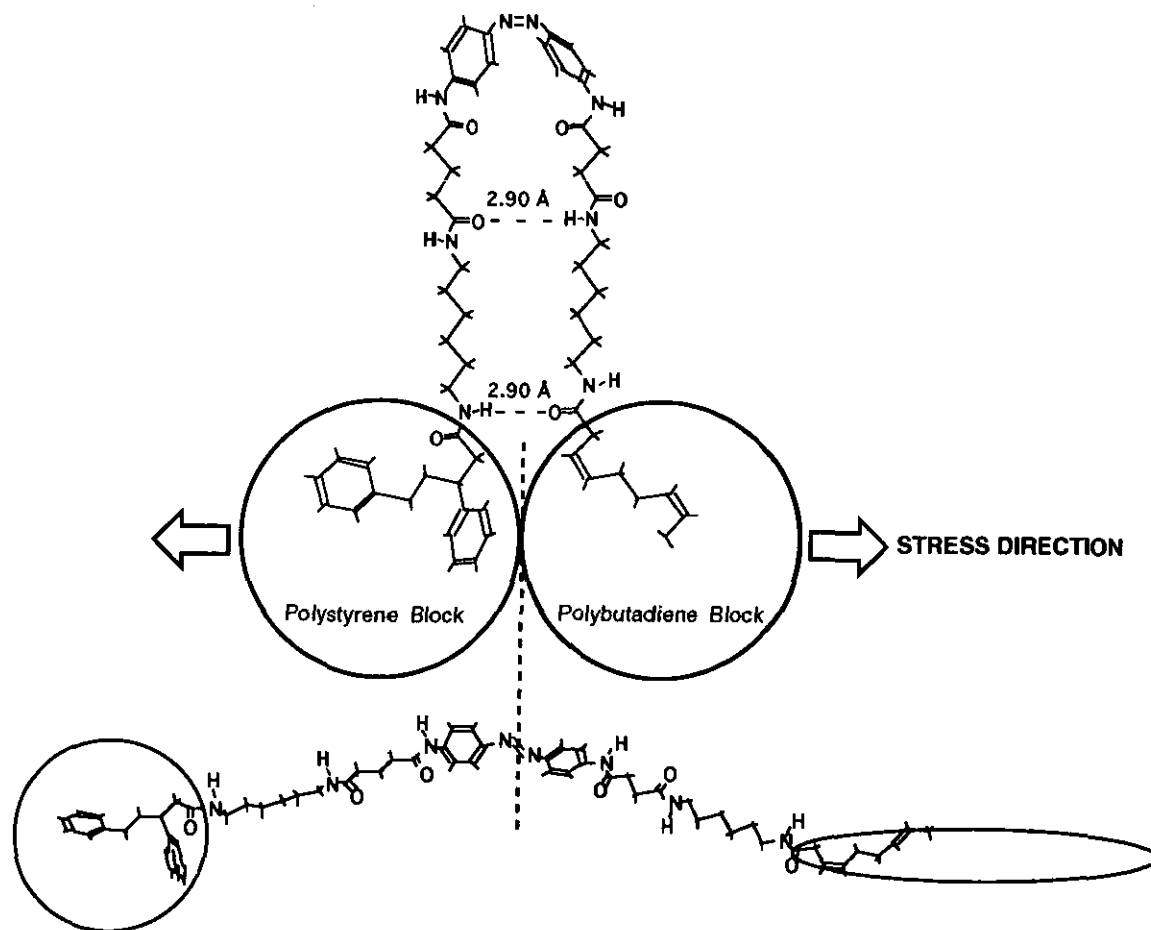


Figure 9. Scale drawing of a 'latched' molecule at an interface between polystyrene and polybutadiene. The changes in shape of the molecule as stress is applied normal to the interface are shown schematically.

7. The oligomeric module for attachment to the matrix

The smart molecule can be attached to the matrix with an oligomer which has the same chemical structure as the polymer used for the matrix, as is the case for the molecule shown in figure 9. In this case, the oligomer is miscible with the matrix, and becomes a part of the matrix during processing of the composite. Alternatively, an oligomer which forms a strong attachment to the surface of the matrix, perhaps by forming a chemical bond, could be used. The length of the attachment and the strength of the individual interatomic interactions can be balanced to adjust the mechanical performance to the design criteria.

8. Nanophase modules

Nanophase modules have the advantage of increasing the concentration of chromophores or other desired chemical species to a level that is easier to observe. Nanophase modules can function as: piezochromic materials; or lead to light-induced mechanical failure, or affect miscibility; or provide 'blurred' interfaces; or provide one or other kind of sensitivity to solvents. Some examples of nano-

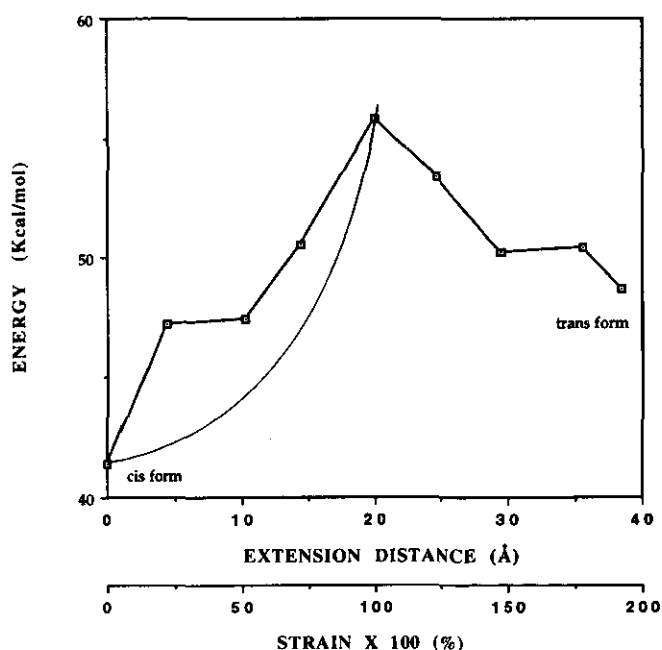


Figure 10. Energy as a function of separation of the chain ends and of strain in the molecule shown in figure 9.

phase modules with interesting and potentially useful properties are described briefly in the following paragraphs.

A polymer-based photorefractive material [14] can be designed with a combination of modular functions associated with nanophase modules. The essential functions include photoexcitation of charge carriers, aligned dipoles to provide an internal field, charge transport, and the ability for the index of refraction to change to follow the pattern of photo-generated charge. Observation of photorefractive effects in a polymer system was reported recently [15].

One kind of interesting nanophase is a crystal that undergoes a melting transition. Polymer molecules incorporated into the crystal at low temperature are released at high temperatures. Strain or stress relaxation phenomena could pull the molecules out of the molten nanophase, so that the material is permanently changed. Mouldable crystal block elastomers provide a familiar macroscopic example of such a material.

Reversible piezochromism in poly(alkylsilanes) was recently reported [16]. Pressures of 4 to 6 kbar produced a shift in an ultra-violet absorption band from around 320 wavenumbers to around 360 wavenumbers in both poly(di-*n*-pentylsilane) and poly(*n*-pentyl-*n*-hexylsilane).

A nanophase module can provide the function of integration. The arrival of small molecules or photons could be integrated until a desired number had arrived, and then a useful chemical transformation could occur.

Amplification can occur in another kind of nanophase system which might utilize a photon to create an acid which would catalyze, for example, the depolymerization of polyoxymethylene by 'unzipping'. This would create a number of formaldehyde molecules which would diffuse with relative ease to other parts of the system and react to produce a colour change, crosslink, or other useful change.

Precipitation and dissolution occurring in the presence of a stimulus could be used to change (rather slowly) from a transparent sheet to a strongly light scattering sheet by creating and dissolving a distribution of nanophase particles with an index of refraction different from the solvent matrix.

9. Summary

The combination of molecular modelling, scanning tunnelling and atomic force microscopy, and state-of-the-art polymer synthesis brings us to a new area. Molecules

of unusual complexity can now be modelled easily and quickly. The parts of these molecules can be synthesized as modules and assembled together using the techniques of contemporary polymer synthesis. Direct observation of molecular scale features with new molecule-resolving microscopes provides other useful information about the design, assembly and performance of these smart molecules. This project brings all these things together. The early results on all three fronts of this project are most promising.

Acknowledgments

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