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# Molecular modelling and graphics of polymers

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*Molecular modelling and graphics studies of polymers have developed as an important tool to predict the performance and design of new polymers. This article reviews the work reported in the literature and compares various commercial packages available in the market. The article also describes  modelling studies carried out on styrene–butylmethacrylate copolymer, and the attempts made to predict the physical properties of the product from the molecular structure.*

COMPUTER-AIDED molecular modelling and graphic visualization of small and large molecules have become a part of chemical research, mainly due to drop in the cost of computing technology, availability of sophisticated graphics software and rapid increase in the cost of conducting laboratory experiments[1]. Modelling and simulation techniques are fairly well established in fields such as biological chemistry and pharmaceuticals. It is now being extended in other areas of chemistry like polymers, materials science and inorganic chemistry.

Polymer molecules are very complex and large, and modelling them invokes a staggering number of variables. This has become feasible over the last few years owing to the increase in available and affordable computer power in the form of graphics work stations

and fast parallel processors. Interest in predicting polymer properties has risen dramatically, especially in industrial laboratories, as the cost of industrial research has increased and as polymers have moved into specialized high-performance areas, named as 'specialty polymers'. Industries are busy creating new 'designer polymers' to meet customer-specific needs. Chemists at Hoechst Celanese are searching for new high-performance polymer blends using modelling and simulation[2]. This approach reduced the number of polymer pairs that needed to be experimentally tested in the laboratory from 300 to 30.

Several companies have joined polymer-modelling consortium established by Biosym Technologies, a software company based in California, to act as a focus for developing new methods in polymer modelling and to distribute them in the form of rigorous software pacakges[1]. The consortium has about 50 members, including Hoechst Celanese, BASF, Ciba-Geigy and Eastmann Kodak. They have released six modules

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related to macroscopic and atomistic approaches to polymer design.

## Literature survey

Several reviews have appeared over the past few years dealing with computer graphics as applied to the field of polymer chemistry, large macromolecules and biopolymers, covering hardware, software and techniques[3-6]. Molecular graphics softwares with limited capabilities and functions are also available[7] for PCs and MACs.

Molecular modelling of polyacrylonitrile, which is used to produce various acrylic fibres, was carried out by Case et al.[8] to determine the spatial arrangement the nitrile group adopts to undergo intramolecular cyclization with the neighbour. They conclude that this idealized cyclization is unlikely to occur due to steric crowding. Modelling is being used to determine the persistent lengths of polymers and hence their potential for liquid-crystalline behaviour[8,9]. Persistence length is difficult to measure experimentally for glassy or molten polymers. Polymers which are strongly constrained to a small number of backbone dihedral angles will be rigid and hard to process. Clarke[9] had modelled the random copolymer formed by hydroxybenzoic acid and hydroxynaphthoic acid at two temperatures and demonstrated from graphics the longer persistence length of the polymer and the enhanced rod-like behaviour at lower temperatures. Interaction between ethylene–vinyl alcohol copolymer and water has been well demonstrated graphically in a study by Case et al.[8].

Energy minimization technique was used to determine the elastic constants of amorphous atactic polypropylene and the agreement[10] with experiment was within 15%. Molecular dynamics technique is found to be generally satisfactory for studying dense polymers in continuous space[11]. Molecular modelling of amorphous polyethylene at 300 K in a unit cell is used to estimate mechanical properties like Young's modulus[9,11]. The value found from the model agrees well with the estimated value for real amorphous polyethylene.

The physical properties of a polymer in a solution are determined by the molecular configurations it assumes. For example, a polymer in a solution that is tightly coiled will have a lower viscosity than when it is extended, because the tightly coiled structure presents a smaller cross-sectional area to the solvent molecules. Bishop et al.[12] investigated the various shapes a polymer chain would take when subjected to Brownian motion and Lennard–Jones forces.

## Comparison of commercial packages

There are a number of high-quality molecular modelling/graphics packages available in the market. The current trend in the modelling field involves replacement of the specialized graphics terminal, connected to a dedicated host computer, by powerful integrated work stations like Silicon graphics, which deliver high-resolution graphics and fast computing. CHEM-X, a software developed by Molecular Design Ltd., Oxford, is the only software that can run on a PC-386 or 486. The capabilities of the major packages for polymer modelling are discussed below.

### SYBYL

This package is supplied by Tripos (a subsidiary of Evans and Sutherland, USA). The polymer module quickly builds, modifies and analyses the properties of both amorphous and crystalline polymers using the rotational isometric state theory. The polymer properties that can be estimated include the end-to-end distance, radius of gyration, persistent vector, elastic constants, fibre modules, thermodynamics, vibrational analysis, electrostatic properties, etc. Systematic random and grid-conformational search options available in the advanced computation module locate the energy minima of a molecule efficiently. The dynamic option simulates molecular motion and exploration of conformational space in systems too large to be solved systematically. The open architecture allows the user to run other in-house softwares or quantum-mechanical programs (MOPAC, MM2, etc.) from the graphics environment interactively.

### QUANTA/CHARMm

This software is supplied by Polygen Corporation, UK. Quanta is a comprehensive package with modules available to study proteins, polymers, inorganics and small molecules. Protein modelling is the main strength of this package. The software has interfaces to X-ray structure interpretation routines. The molecules can be constructed in QUANTA by linking fragments together rather than by the free sketching approach in SYBYL. It can generate structural data in all molecular formats. Interactive access is provided to the CHARMm energy calculations program for carrying out energy minimization and molecular dynamic simulations. Molecular force field technique is used to calculate the conformational energy. QUANTA like SYBYL has an open architecture.

### CERIUS

This is supplied by the Cambridge Molecular Design, a company which has merged with BIODESIGN to form Molecular Simulations Incorporated. CERIUS is a uni-

que package oriented towards materials science. It is not a complete modelling package, but a specialized tool for addressing inorganic, polymer, crystals and fibre structures. It can be used to predict the properties of polymers by statistical mechanics methods. It contains methods which calculate the interactions between molecular entities and minimizes these energies with respect to the molecular features.

No sketch is available, but the build option for molecules is centred around the construction of polymers and crystals. Surfaces may be displayed by simply specifying the Miller indices. CERIUS reads and writes a number of standard formats; this allows easy communication between CERIUS and other molecular modelling packages.

## CHEM-X

This is a modular package which can be expanded to include modelling of inorganics, polymers and proteins. Sketch and build facilities are similar to those of QUANTA and the resulting molecule can then be minimized through molecular mechanics methods based on MM2 parameter types. The quantum mechanics module is very extensive, with interfaces to all major QM codes. The MOPAC interface is highly comprehensive. Regular, block and random copolymers can be built automatically from a library of monomers. Mixed copolymers can be built taking into account multiple head and tail connection points to form branching and star polymers. Atactic, isotactic or syndiotactic polymers may also be constructed. Interaction of the polymer chain with crystal faces and identification of low-energy conformations can be carried out. Polymer properties can be determined by statistical mechanical approach. Temperature-dependent properties like heat capacity, average chain length, etc., can also be estimated for crosslinked polymers.

## INSIGHT/DISCOVER

This software package is supplied by Biosym Technologies. INSIGHT is the 3D modelling backbone and DISCOVER the mechanics/dynamics package. The model building and energy minimization is similar to QUANTA and CHARMm. The polymerizer module can be used to build homopolymers and copolymers based on conditional probabilities or reactivity ratios and monomer concentrations. Many submodules are available to calculate the properties of amorphous polymers, thermoplastics, copolymers and polymer blends and solutions. The bipolymer module can be used to model RNA, DNA and peptides.

## Molecular modelling – A case study

In this article the molecular modelling and graphics of an industrially important specialty copolymer, namely styrene–butyl methacrylate, is described with the following in view: (i) explain the general methodology adopted in modelling of polymers, (ii) information that could be obtained from the visualization of this macromolecule, (iii) predict its physical properties, and (iv) possible steric effects that come into play during its formation from individual monomers. Modelling a small portion of the polymer does not describe fully the polymer properties, but nevertheless, is able to explain some of the observed characteristics.

## Methodology

Molecular modelling and graphics studies were carried out on an IRIS 3100 work station using QUANTA2/CHARMm softwares. The methodology adopted to calculate the conformational energy of polymers is similar to the molecular force field techniques developed by Levitt[13]. The actual molecular force fields used in the empirical energy calculations are a set of analytical expressions to derive individual energy terms in the following equations:

$$E_{total} = E_{bond\ stretch} + E_{angle\ bending} + E_{dihedral}$$
$$+ E_{Vanderwaals} + E_{out\ of\ plane} + E_{electrostatic}$$

Each of the terms in this equation is estimated using the procedure outlined by Levitt.

The preferred molecular structures are determined by minimizing the energy with respect to the atomic coordinates. There are a number of energy algorithms available in CHARMm for energy minimization. The two techniques used in this work are the steepest descent method and Powell's conjugate gradient method[14]. For small molecules, a global minimum-energy conformation is often found, whereas for large macromolecular systems, energy minimization allows one to examine the local minimum around a particular conformation. Later, the conformational search facility available in QUANTA is used to sample the space for determining alternate conformations of the molecular structure and their energies. The techniques available here are grid search, Monte Carlo sampling of conformational space, and CHARMm minimizations on a set of randomly generated structures. The last two techniques were used in our study to determine the minimum-energy conformation of the macromolecule.

## Results and discussion

Styrene–n-butyl methacrylate copolymer finds application in a wide range of specialty products, namely in
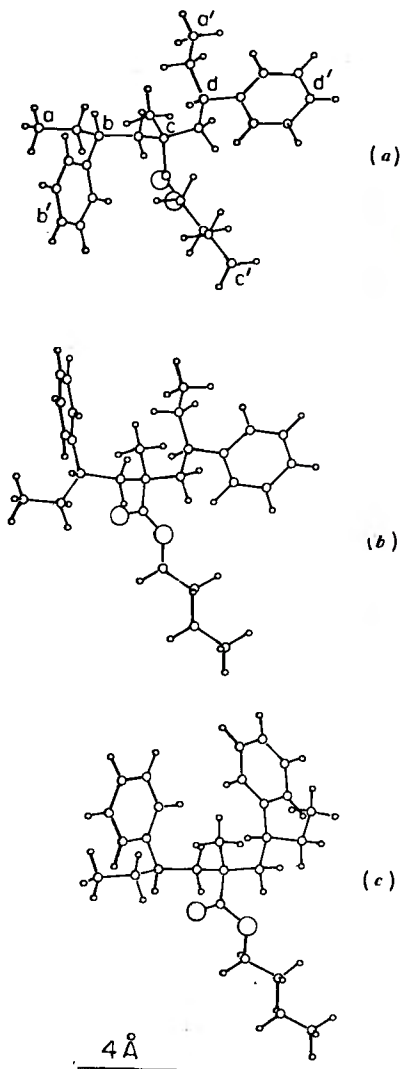
**Figure 1.** Minimum-energy molecular conformation of one-styrene-two-BMA units represented by the ball-and-stick model: (*a*) isotactic (*b*) syndiotactic, and (*c*) atactic conformation (H represented by the smallest-sized circles, O by the largest circles and C by the intermediate-size circles).

**Table 1.** Distances of atoms (Å) for three conformations given in Figure 1 for styrene–BMA copolymer

|            |      | *a*   | *b*   | *c*   |
|------------|------|-------|-------|-------|
| (end to end) | aa'  | 7.14  | 8.06  | 8.99  |
|            | bc   | 2.67  | 2.75  | 2.69  |
|            | cd   | 2.69  | 2.71  | 2.68  |
|            | bd   | 4.48  | 4.46  | 4.57  |
|            | b'c' | 8.66  | 12.53 | 12.51 |
|            | c'd' | 7.45  | 8.66  | 11.73 |
|            | b'd' | 11.61 | 10.37 | 5.87  |
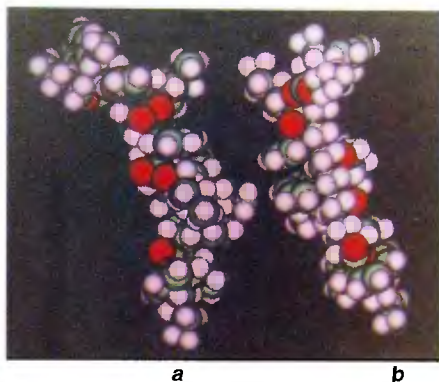


**Figure 2.** Minimum-energy molecular conformation of styrene–BMA copolymer consisting of six styrene and five BMA molecules: *a*, isotactic and *b*, atactic (colour code: green, carbon; red, oxygen; white, hydrogen). (In isotactic conformations the phenyl and *n*-butyl groups are on the same side of the backbone, and in atactic the functional groups are present on both sides of the backbone.)

the area of reprographics. This copolymer is prepared in a suspension mode, with the polymerization reaction being initiated by benzoyl peroxide[15]. A similar methodology is adopted in the preparation of other copolymers like styrene–methyl methacrylate and styrene–butyl acrylate, etc. These polymers have important applications because of their mechanical, dielectric, flow and thermal (softening) properties. These physical properties are determined by several factors, e.g. configuration of the polymer chain, monomer sequencing and the conformations adopted by each monomer with respect to the other.

Figure 1 shows the three minimum-energy conformations of a copolymer of styrene and *n*-butyl methacrylate (BMA), namely (*a*) isotactic, where both the benzene rings of the styrenes on the two sides of BMA are on the same plane as the butyl group of BMA, (*b*) syndiotactic, where only one benzene ring of styrene is on the same plane as the butyl group, and (*c*) atactic.

where none of the benzene rings of styrene are on the same plane as the butyl group. Table 1 gives the distances of the various carbon atoms as measured from molecular graphics for the three configurations. The end-to-end distance of one unit is 7.14, 8.06 and 8.99 Å, respectively, indicating that each unit of isotactic configuration is compact, while one unit of atactic is spread out. Extended-chain conformation is generally expected to offer more viscosity in solution than a compact chain, since it offers more cross-sectional area to the solvent molecule. Moreover, it will also enhance the glass transition temperature. The benzene-to-benzene distance is longest in the case of isotactic and shortest in the case of atactic configuration. Also, the minimum energies estimated from energy minimization are 12.9, 5.0 and 10.5 kcal mol$^{-1}$ for isotactic, syndiotactic and atactic configurations, respectively, indicating that syndiotactic configuration is the most probable one. The end-to-end distance for a chain consisting of six styrenes and five BMA molecules in minimum-energy conformation is estimated to be 25.2, 26 and 26.4 Å for isotactic, syndiotactic and atactic conformations, respectively. Figure 2 shows a photograph of the isotactic and atactic copolymer.

## Conclusions

Molecular graphics of polymers has increased the understanding of chemists regarding the conformation and behaviour of polymer molecules. It is a relatively new area for industrial laboratories and can enhance the understanding of the existing polymer systems that are produced, leading to the development of new systems. In addition to modelling the behaviour of polymers, it is also possible to gain an insight into their synthesis. The stereochemical control of chain growth polymerizations can be modelled to understand its root cause. The use of simple molecular mechanics programs to visualize the possible approach route of the monomer to the chain end can give important clues to its growth.

Some commercial softwares are available which can be used for building block or random copolymers, calculating statistical thermodynamics, and predicting their properties, including elastic constant and phase transition temperatures. Polymers could also be built with different configurations and conformations, as has been demonstrated in the case of styrene–butyl methacrylate system.

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