

REPORT DOCUMENTATION PAGE

AD-A218 891

1b RESTRICTIVE MARKINGS  
NONE

3 DISTRIBUTION/AVAILABILITY OF REPORT  
Approved for public release.  
Distribution unlimited. (2)

4 PERFORMING ORGANIZATION REPORT NUMBER(S)  
Technical Report No. 21

5 MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION  
Massachusetts Institute  
of Technology

6b OFFICE SYMBOL  
(if applicable)

7a. NAME OF MONITORING ORGANIZATION  
ONR

6c. ADDRESS (City, State, and ZIP Code)  
77 Massachusetts Avenue, Room 1-306  
Cambridge, MA 02139

7b. ADDRESS (City, State, and ZIP Code)  
800 North Quincy Street  
Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING  
ORGANIZATION  
DARPA

8b. OFFICE SYMBOL  
(if applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER  
N00014-86-K-0768

8c. ADDRESS (City, State, and ZIP Code)  
1400 Wilson Boulevard  
Arlington, VA 22209

10 SOURCE OF FUNDING NUMBERS  
PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.  
R & T Code A 400005

11. TITLE (Include Security Classification)  
SIMULATION OF INELASTIC DEFORMATION IN GLASSY POLYPROPYLENE AND POLYCARBONATE

12. PERSONAL AUTHOR(S)  
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13a. TYPE OF REPORT  
Interim Technical

13b. TIME COVERED  
FROM 1988 TO 1989

14. DATE OF REPORT (Year, Month, Day)  
1989 December 1

15. PAGE COUNT  
2

16. SUPPLEMENTARY NOTATION  
Abstract of presentation at the ACS Symposium on Computer Simulation in Boston on  
April 23-27, 1990

17 COSATI CODES table with columns FIELD, GROUP, SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)  
Plastic flow mechanisms; glassy polymers; segment rotations; computerized simulations; molecular interactions; molecular structure; (KT)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)  
A brief summary of research on the simulation of plastic deformation in computer generated glassy polypropylene, and polycarbonate. Determination of the stress-strain response, and elucidation of the molecular segment motions associated with such deformations. Determination of the kinematics and energetics of phenylene ring rotations and carbonate group motions in polycarbonate. Keywords:

DTIC ELECTE MAR 05 1990 stamp

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT  
 UNCLASSIFIED/UNLIMITED  SAME AS RPT  DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION  
Unclassified

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## SIMULATION OF INELASTIC DEFORMATION IN GLASSY POLYPROPYLENE AND POLYCARBONATE

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### INTRODUCTION

The molecular mechanisms of both large strain plastic deformation and those encountered in internal friction in flexible chain plastic polymers have remained controversial at best. While many ad-hoc mechanisms of imagined molecular conformational changes [1-5] have been advanced and have proved to be very useful as kinetical scaling laws [1,4], there has been considerable skepticism on their validity. To remove this controversy we have performed detailed computer simulations of such deformations on bona-fide molecular structural models of glassy polypropylene (PP) obtained earlier by Theodorou and Suter (T & S) [6-8], and on bisphenol-A polycarbonate (PC) which we have newly determined. Here we report the results of these simulations.

### THE MOLECULAR STRUCTURE MODELS

The molecular structure model used for glassy PP was that of T & S [6], for glassy atactic PP of a degree of polymerization of 76, at a density of 0.892 g/cm<sup>3</sup>, appropriate for a temperature of 233 K, and in the form of cubes of 18.2 Å on the side, subject to periodic boundary conditions.

The molecular structure of glassy PC was obtained by a similar approach of a static energy minimization scheme [9,10] and was for a PC molecule with a degree of polymerization of 34, containing 485 atoms, in the form of a cube of 18.44 Å on the side, having periodic boundary conditions and at a density of 1.2 g/cm<sup>3</sup>, appropriate for 295 K.

The molecular structure of one specific configuration of PC is shown in Fig. 1, where the atoms are shown reduced to about 1/3 of their size to permit viewing into the structure.

### PLASTIC STRAINING OF POLYPROPYLENE

For all stages of plastic deformation atomic site stress tensors were calculated for each atom by the generalization of T & S [6] of the earlier Born and Huang [11] definition, given for the *i*th atom by:

$$\sigma_i^{\alpha\beta} = -\frac{1}{2V_i} \sum_{j \neq i} \left[ r_{ij}^{\alpha} F_{ij}^{\beta} + \sum_{\gamma} \epsilon^{\alpha\beta\gamma} \frac{T_{ij}^{\gamma}}{2} \right] \quad (1)$$

where  $\alpha, \beta$  and  $\gamma$  are cartesian indices, *i* and *j* are indices of specific atoms,  $r_{ij}$  is the radius vector connecting atoms *i* and *j*,  $F_{ij}^{\beta}$  and  $T_{ij}^{\gamma}$  are the  $\beta$  and  $\gamma$  components of the force and torque vectors acting between atoms *i* and *j*, while  $\epsilon^{\alpha\beta\gamma}$  is the permutation tensor, and  $V_i$  is the van der Waals volume of atom *i*. Corresponding to the stresses atomic site strain increments were also defined based on the increments of the displacement gradients of each atom in relation to its immediate neighborhood. The elements of this strain increment tensor are (for infinitesimal increments):

$$\Delta \epsilon_i^{\alpha\beta} = \frac{1}{2} \left[ \frac{\partial \Delta u_i^{\alpha}}{\partial x^{\beta}} + \frac{\partial \Delta u_i^{\beta}}{\partial x^{\alpha}} \right] \quad (2)$$

Of particular interest were the trace and deviatoric parts of the stress and strain increment tensors, giving the atomic site negative pressure  $\sigma$ , von Mises shear stress  $\tau$ , the atomic site dilatation  $\Delta \epsilon$ , and the work equivalent shear strain increment  $\Delta \gamma$ , defined as:

$$\sigma = \frac{1}{3} \text{Tr}(\sigma) \quad \tau = \frac{1}{2} \text{Tr}[(\sigma - \sigma I)^2]^{1/2} \quad (3,4)$$

$$\Delta \epsilon = \frac{1}{3} \text{Tr}(\Delta \epsilon) \quad \Delta \gamma = \frac{3}{2} \text{Tr}[(\Delta \epsilon - \Delta \epsilon I)^2]^{1/2} \quad (5,6)$$

To strain the initially 18.2Å simulation cell of PP under a constant volume constraint, tensile strain increments of  $2 \times 10^{-3}$  and two associated transverse compressive strain increments of  $10^{-3}$  were imposed on the cell. All atoms inside the cell were given similar affine displacements followed by re-minimization of the energy of the entire structure.

### RESULTS OF PLASTIC STRAINING OF PP AND DISCUSSION

Figure 2a shows the tensile stress-strain curve of a single configuration deformed to a total strain of 0.2. Because of the very small size of the cube, it contains a substantial level of atomic "stress noise," so that in the initial state the tensile stress is not zero. Subsequent deformation steps elicit a protracted anelastic response which is typical of glassy structures [12], and is most likely associated with very short range segment relaxations. Once this anelasticity is completely polarized out, the structure responds in a series of clearly delineated cycles of elastic loading followed by plastic "collapse" as is shown at b, d, e, f, and g. Deformation prior to a plastic collapse exhibits complete elastic reversibility while reversal of strain after a plastic collapse is also elastic but at the newly lowered level of stress.

When the responses of 9 separate configurations are combined as in Fig. 2b, the level of stress noise is very substantially reduced, and the initial tensile response is more nearly linearly elastic. Once yielding occurs at a strain level of about 0.05 the stress strain curve continues to exhibit individual uncorrelated plastic collapse events. Figure 2b also shows that during plastic straining at constant volume the pressure is steadily increasing indicating the dilatant nature of the plastic deformation in the glassy PP.

From detailed examinations of many stereo pairs of the changing molecular conformations during a typical plastic collapse event what could be gleaned was relatively small disorderly displacements of segments, resulting roughly in a quasi-uniform small plastic strain increment over the entire simulation volume. Since the plastic collapses occur at a constant total strain the elastic stress drops,  $\Delta \sigma$ , can be directly related to plastic strain increments,  $\Delta \epsilon_p$ , by:

$$\Delta \epsilon_p = -\frac{\Delta \sigma}{E} \quad (7)$$

Figure 3 shows both the cumulative distribution and the frequency distribution of these plastic strain increments. The average magnitude of these strain increments, when converted into shear strain is  $\Delta \gamma^* = 0.037 (\pm 0.035)$ . These are nearly an order of magnitude smaller than what the earlier ad-hoc models had considered, where it had usually been assumed that relatively large displacements occur among relatively small groups of molecular segments. The principal finding of our simulation is an inverted picture in which a plastic relaxation event consists of a relatively small transformation shear strain in a relatively large volume element. This is most clearly demonstrated when the simulation results are compared with the measurements of the activation volumes  $\Delta v^*$  which is a product of the local shear strain increment  $\Delta \gamma^*$  and the size of the local volume  $\Omega$  in which a thermally activated unit plastic relaxation event occurs, i.e.,

$$\Delta v^* = \Omega \Delta \gamma^* = kT \left( \frac{\partial \ln \dot{\gamma}}{\partial \sigma} \right)_{p,T} \quad (8)$$

Table I gives the activation volumes measured by Argon and Bessonov [4] in six glassy polymers. If the transformation shear strains of our simulation in PP are taken as typical for most glassy polymers, it is possible to calculate estimates of the sizes of the local volumes undergoing a unit plastic relaxation event. Table I shows that these local volumes are very large indeed, being typically 40 - 60 Å on the side. Clearly, this is a direct consequence of the relative inextensionality of backbone bonds and inflexibility of bond angles, requiring that all shear strains develop inside this large volume element by a series of successive bond rotations that must average out over the volume to a value no larger than the overall shear strain increment in the volume.

### ROTATIONS OF PHENYLENE RINGS AND CARBONATE GROUPS IN PC

Stress induced rotations of phenylene rings and perhaps carbonate groups have often been suspected as sources of the  $\beta$  internal friction peak in PC. To explore this possibility most phenylene rings in the simulation structure were incrementally rotated, followed by fixing one or the other of the torsion angles on either side of the rotated phenylene ring, and by re-minimizing the system energy. Such a ring that is being rotated is identified in Fig. 1 in black. In both cases the total energy of the system increased stably and reversibly to a peak value where upon it dropped suddenly to a lower level. Depending on whether the torsion angle between the ring and the carbonate group or between the ring and the isopropylidene group had been fixed, two generically different responses were found. In the first case the drop in energy was associated with a complete "flip" of the phenylene ring that was being rotated while in the second case a clear conformational change in the neighboring carbonate group was found. In

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## SIMULATION OF INELASTIC DEFORMATION IN GLASSY POLYPROPYLENE AND POLYCARBONATE

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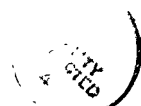
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