# Dimensional and volumetric changes in cylindrical rods of polymers subjected to a twist moment

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The dimensional and volumetric changes which accompany torsion of a cylindrical specimen have been measured, for the first time, in a wide variety of polymers by subjecting the specimens to a twist moment. It was found that the twisted polymers developed widely different amounts of dimensional and volumetric change, but the change in length was always positive (elongation) whereas the change in diameter was always negative (contraction), a feature which appears to be shared by many solid substances. The volume always contraced in most polymers except Celcon, an acetal copolymer, which underwent steady expansion, and PMMA which expanded somewhat before undergoing contraction. To our knowledge, volumetric contraction in torsion has not been observed previously in solid substances.

**Keywords** Torsion, dimensional changes; second-order effects; volumetric changes; shear stress

It is well-known[1–6] that the mechanical behaviour of polymeric solids is highly sensitive to changes of volume during deformation. This volume effect, which often causes the mechanical property to deviate from a linear relationship (between stress and strain), is manifested not only in relaxation and creep tests[4,5], but also in tests performed under a constant rate of strain[1–3,5–7]. In simple tension tests, for example, it has been shown[5,7] that a gradual softening and yielding of the polymers can be accounted for by considering the increase in free volume associated with the strain-induced dilation. Despite the importance of the volume effect, however, measurement of dimensional and volumetric changes has rarely been performed in conjunction with the mechanical tests, and in cases where this is done, it has been limited mostly to tests performed under simple tension or simple compression[1,6].

Information on dimensional changes in torsion of a cylindrical rod is especially important since, as is well known[8,9], these changes represent entirely nonlinear mechanical effects. Consequently, data for dimensional and volumetric changes obtained from torsion tests† are useful not only for assessing the influence of volume change on torsion behaviour, but also for extracting the information that can be attributed entirely to the nonlinear effects. In this communication we wish to report the highlights of such a study made on a wide variety of polymers and, in particular, describe the first observation of torison-induced volume contraction in solid substances.

Specimens used in this study were 1.27 cm ($\frac{1}{2}$ inch) diameter cylindrical rods made of polycarbonate, PC (Merlon 60, Mobay Chemical Co.), cast poly(methylmethacrylate), PMMA (Polymer Corp.), poly(tetrafluoroethylene), PTFE (Teflon, E. I. du Pont de Nemours and Co.) and Celcon, an acetal copolymer made by Celanese Plastics Co. Specimens made of other polymers (high and low density polyethylenes, polypropylene, nylon-6,6 and acrylonitrile-butadiene-styrene or ABS) were also tested but, for the sake of brevity, only those results pertinent to our discussion will be described. The rods were each cut into a length of 18.5 cm, annealed at different temperatures (70°C for PMMA and ABS and 120°C for other polymers) for 16 h and cooled down slowly to room temperature in 5 h.

Torsion tests were performed in an Instron tester (model TT-D) equipped with a torsion accessory (Instron G-70-1) which allowed the 'free' end of the specimen to move only along its length while the specimen was being twisted at an angular speed of $5.6 \times 10^{-3}$ rad s$^{-1}$. Changes in specimen diameter were measured by a high sensitivity transverse strain sensor (Instron, G57-11) attached to the middle of the specimen while changes in the specimen length were measured by a pair of dial gauges which were placed near one end of the specimen at 180° interval to detect the axial movement of one specimen grip relative to the other. Details of the experimental procedure will be presented in the future in a more comprehensive report. Six specimens of each polymer were used in the test for the purpose of data averaging.

*Figure 1* is a plot of the torque-twist data up to a twist angle, $\psi$, of 0.62 rad cm$^{-1}$. Occasional inspection of specimens during the test showed that all polymers (including those not shown in *Figure 1*) deformed uniformly until they yielded or fractured (PMMA). Upon yielding, however, the PC and ABS specimens developed localized shear bands while the other polymers continued to deform uniformly until the tests were terminated at a twist angle of about 0.65 rad cm$^{-1}$. Consequently, dimensional measurements of PC and ABS specimens were terminated when they reached the yield points. It can be seen from *Figure 1* that the torque-twist curves are not linear even in the range of $\psi$ where the polymers are still within the yield limit or the point of fracture. Sincy symmetry considerations (i.e., a negative torque produces a negative angle of twist) require the torque to be an odd function of $\psi$, this indicates that the nonlinearity in the

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† A distinction should be made here between the commonly known simple torsion and torsion under a twist moment. The former refers to a state of deformation (simple shear) for which the corresponding stresses are to be found, whereas the latter refers to a system of tractions under which the deformation in the body is to be determined. The two problems are different in nonlinear mechanics. We note also that almost all torsion tests performed in practice are of the latter category since simple torsion tests are difficult to perform in nonlinear compressible materials, as shown by Rivlin[8] and Murnaghan[9].

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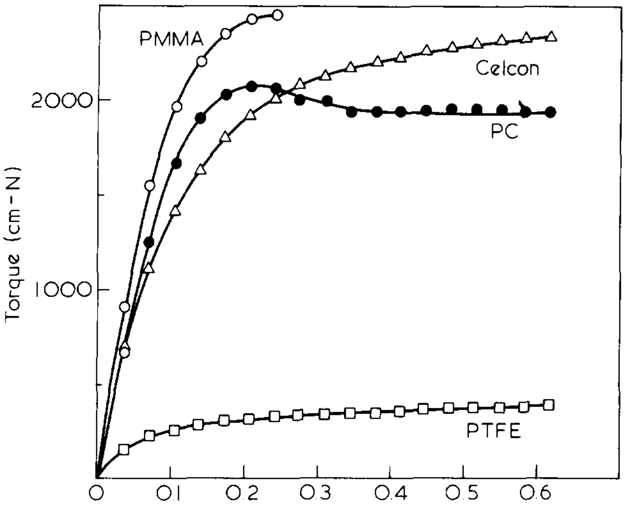

*Figure 1* Plot of torque vs. angle of twist, $\psi$, for PMMA, PC, Celcon and PTFE

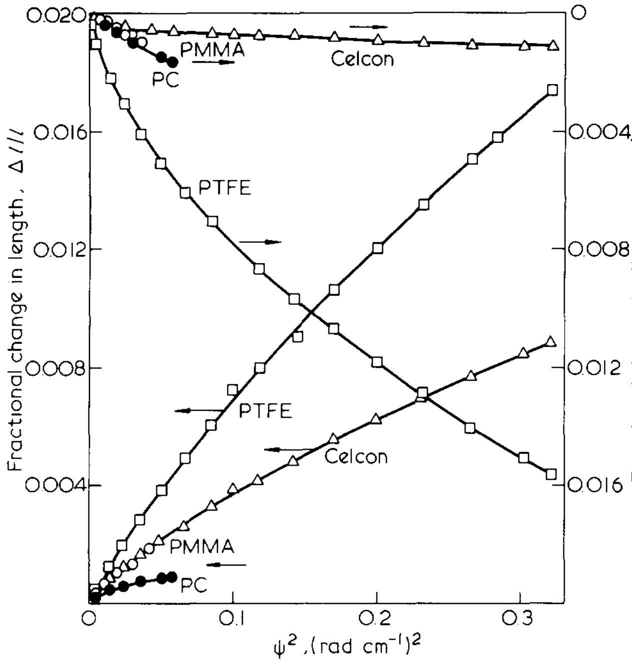

*Figure 2* Plots of fractional changes in length and diameter as functions of square of twist angle, $\psi^2$

torque-twist behaviour is at least of the third order (as measured by a power series expansion of the torque-twist function with respect to $\psi$)[8,9].

The fractional changes in length ($\Delta l/l$) and diameter ($\Delta d/d$) during torsion are shown in *Figure 2*. Since the changes represent the responses due to second or higher order effects[8,9], these data have been plotted as function of $\psi^2$. Several features are evident in *Figure 2*. First, although the length and diameter behaviour varies widely from polymer to polymer, the change in length is always positive (elongation) whereas the change in diameter is always negative (contraction). This characteristic appears to be shared by a wide class of materials since tests performed on metals[10,12,13] and rubbery materials[10,14] have also shown the same length elongation and diameter contraction behaviour. Secondly, as with the torque-twist curves (*Figure 1*), the plots for $\Delta l/l$ and $\Delta d/d$ are all nonlinear, indicating that dimensional behaviour is also sensitive to nonlinear effects of orders higher than the second.

Finally, examination of the changes in length and diameter of individual polymers reveals that polymers showing a large axial elongation do not necessarily develop a correspondingly large contraction of diameter. For example, Celcon elongates almost twice as much as PC at any angle of twist, but its diameter contracts very little in comparison with PC. This is a clear indication that some of the polymers have undergone volume change during torsion.

In *Figure 3*, the fractional changes in specimen volume, $\Delta V/V$, calculated from the data of length and diameter measurements (*Figure 2*), are plotted as function $\psi^2$. While the results of other polymers are not shown here, all of them were found to fall within the bounds represented by the four polymers shown in the figure. The most striking feature of the plots is the sign of the volume change which is always positive in Celcon and always negative in the other polymers (including those not reported here); one possible exception is PMMA which might have expanded slightly before undergoing contraction. Although volumetric changes in a cylinder subjected to torsion have been investigated, to our knowledge, this is the first instance in which the negative expansion behaviour has been observed. For example, Poynting (ref 10, pp. 397 and 424) measured the dimensional changes during torsion in wires of steel, copper and India-rubber, and found them to either undergo expansion (steel and copper) or show a little change in volume (India-rubber).

In his interpretation of the torsion data, Poynting[10] drew an analogy between torsion of a cylindrical rod and shear of a cubical solid[14], and ascribed the dimensional and volumetric changes to the high-order effects of shear stress which induces normal stresses in both the radial and axial directions. However, Poynting's use of torsion-shear analogy appears to be in error since, according to the elastic torsion analysis of Rivlin[8], the twist moment induces not only the normal stresses in the radial and axial directions but also a body force in the radial direction.

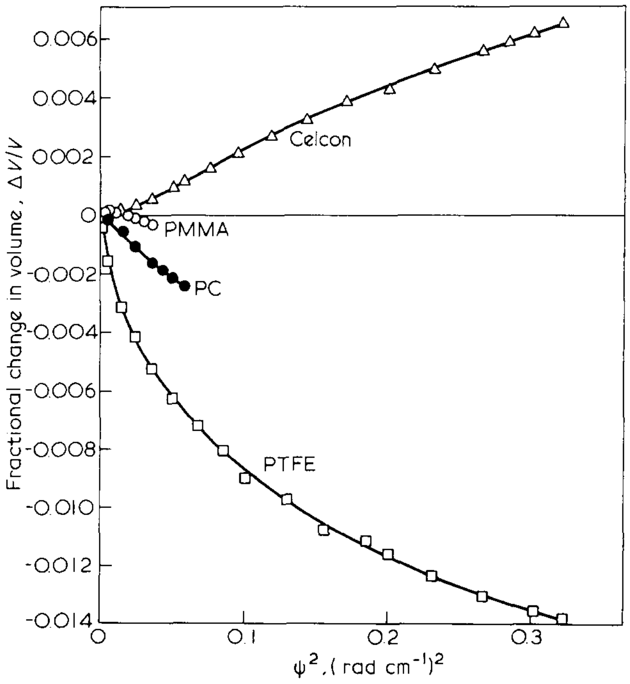

*Figure 3* Dependence of fractional changes in volume on the square of twist angle, $\psi^2$

Consequently, the material elements in the twisted specimen are subjected to a state of secondary stresses which are more complex than those arising from shearing of a cube[14], and it is probably these secondary stresses which are responsible for the dimensional and volumetric changes observed by Poynting and by us in metals and polymers. However, while the dimensional and volumetric behaviour in torsion may be accounted for by the nonlinear character of the material, it remains unclear why metals undergo expansion while most of the polymers develop contraction of volume. We wish to pursue this subject further in a future study.

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# A kinetic study of the interactions of *trans*-polyacetylene $(CH)_x$ with oxygen

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The kinetics of doping and degradation of all *trans*-polyacetylene by oxygen, have been studied over the temperature range 70°–110°C. Doping and degradation have first-order kinetics with the observed Arrhenius parameters $E = 11.52$, $E = 13.45$ kcal mol$^{-1}$ and log $A$ (s$^{-1}$=4.19, log $A$ (s$^{-1}$)=4.49 respectively. The observations support the view that the reactions proceed *via* an intermediate-complex mechanism. Initially oxygen reduced the resistivity of $(CH)_x$ by formation of a charge transfer complex and subsequently reacted with $(CH)_x$ with an increase in resistivity.

**Keywords** Polyacetylene; kinetics; oxygen; doping; degradation

## *Introduction*

Polyacetylene $(CH)_x$ is a unique material of considerable technological interest. Upon doping with both electron donating or accepting species, its electronic transport properties cover the entire range from insulators to semi-conductors and metals[1,2]. However, both pure and doped $(CH)_x$ are sensitive to air and oxygen. In particular the mechanical[3], electrical[4] and magnetic properties[5,6,7] of $(CH)_x$ can be drastically modified by contact with oxygen.

It has been reported that exposure of polyacetylene to oxygen for a longer period caused irreversible chemical changes in the material (compressed powder pellets) but complications arose in the extrapolation of continuous films[8].

The kinetics of doping and degradation of polyacetylene with oxygen were studied by Pochan *et al.*[9] with various *cis–trans* compositions at elevated temperatures. They reported that the kinetics of the degradation is first-order leading to consecutive reactions. However the thermal behaviour of the intermediate complex and the thermodynamic parameters were not studied in detail. After plotting $\log\frac{R_t}{R_0}$ against time, these authors obtained a curve which gave two different straight lines, i.e. two different rate values probably related to the various transformations of polyacetylene (*cis* to *trans* isomerization, doping and degradation processes). To avoid the effects of *cis* to *trans* isomerization on the kinetics, only pure *trans* $(CH)_x$ was used here and thus this study is related to the effect of oxygen on *trans* $(CH)_x$.

## *Experimental and Results*

For all the experimental runs, the polyacetylene used was prepared by a modification of the method described by Ito *et al.*[10] using a Ziegler–Natta catalyst. The *cis* rich $(CH)_x$ obtained was heated to give *cis* to *trans* isomerization at 150°C for 30 min. All-*trans* films of thickness *ca* 100 $\mu$ were used in this investigation.

The reaction was studied in the following manner: in a reactor the Pt-electrodes were kept vertical, sealed in a

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