Observation of Molecular Chain Scission during Crazing of Polystyrene

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A series of gel permeation chromatographic (GPC) separations has been performed on polystyrene specimens in an attempt to discern whether or not mechanical crazing is accompanied by significant covalent bond scission. It was found that the extent of scission is not large but is indeed present in concentrations that are detectable by GPC. This suggests that molecular-slippage-only models of the crazing process are perhaps overly idealized and that crazing cannot take place in highly entangled polymer solids without some bond rupture.

INTRODUCTION

Crazing is well-known to be an important yielding and fracture mechanism in amorphous polymer glasses, and may also be of significance in many other types of polymers, as well (1). Crazes are similar to cracks in that they represent stress-induced discontinuities in the material that grow away from points of stress concentration along directions transverse to the principal normal stress. They differ from cracks, however, in that they contain fibrils of oriented (and thus, strengthened) material that bridge the craze region and provide a mechanism for stress transmission. In many instances, they must be regarded as dangerous, since they act as crack precursors and precede the catastrophic fracture of the specimen. In some other cases, such as the rubber-modified polystyrenes, the energy absorption accompanying craze formation is used to advantage to improve impact behavior.

Due to the work of Sternstein (2) and others, crazing is generally regarded as a mechanism consisting predominantly of molecular chain slippage: the mobility of the material is enhanced by an environmental swelling agent or by the dilatational component of the applied stress, and the deviatoric component of the stress state then induces flow. Attempts to model this process have generally neglected chain rupture and concentrated on chain slippage (see Ref. 3, for instance), but it seems inevitable that some chain scission must accompany such a large-scale rearrangement in a highly entangled polymer solid. Elucidation of the extent of scission may help in the development of more realistic models of the crazing process and, at the very least, should improve our intuitive understanding of this important mechanism.

In recent years, several different techniques of analytical chemistry have been used to assess the extent and kinetics of chain scission in polymers undergoing mechanical damage. The most popular of these techniques has been electron spin resonance (ESR) spectroscopy, which is able to monitor the number of scission-induced free radicals resulting from homolytic scission of covalent bonds and is also able to identify their local chemical environment by means of their hyperfine structure (4). This technique has certain limitations that prevent its easy application to crazing studies, however. The radicals must be sufficiently stable to permit detection, and the damage must be dispersed throughout the specimen in high enough concentration to exceed the sensitivity limit of the ESR spectrometer. Further, the possibility of extensive secondary radical reactions following chain scission often makes ESR observations ambiguous. To date, no successful ESR measurements of bond rupture in crazed polymers have been reported. This null result has been cited (3) in support of slippage-only models of crazing but, in light of the limitations of ESR, should not be taken to exclude the possibility of chain rupture.

Other techniques for detection of chain scission are generally less sensitive than ESR but are often less ambiguous, in that they measure effects that are related directly and irreversibly to chain damage. This paper reports results of gel permeation chromatography (GPC) applied to virgin and crazed polystyrene, and demonstrates that detectable chain scission does indeed accompany crazing in this material.

EXPERIMENTAL

Polystyrene sheet specimens approximately 0.5 mm thick were obtained by cutting from commercially available beverage containers. These specimens were originally intended only as a means of operator training on the chromatograph and were therefore not subjected to a thorough characterization. Nevertheless, it is felt that the results to be reported below will be applicable to a variety of polymer glasses regardless of their detailed formulation. It was found that a high craze density could be developed by manual flexing without

RESULTS AND DISCUSSION

In *Fig. 2*, the ratio C/C_o, is plotted *vs.* $x/s(t)$, with γ as a parameter for $\beta = 1$*. As can be seen from this graph, concentration distribution curves for $\gamma > 0$ (i.e., concentration-dependent diffusivity) are markedly different both quantitatively and qualitatively from the one obtained for $\gamma = 0$ (i.e., constant diffusivity). For example, in the case of $\gamma = 0$, the concentration gradient is steeper at $x = 0$ (i.e., surface of the polymer) than $x = s(t)$ (i.e., boundary between glassy and rubbery regions). However, for cases $\gamma > 0$, the reverse is true.

It is interesting to note that the concentration distribution approaches almost a step change for $\gamma = 10$. Therefore, the existence and the position of the sharp advancing boundary can be partially attributed to the strong concentration dependency of diffusivity. To test the reliability of the method used in calculations, exact and approximate solutions are compared for the case of constant diffusivity; the results for $\beta = 1$ are given in *Table 1*.

*Results for β values of 0.2, 0.5, and 2.0 are available from the authors on request.

NOMENCLATURE

A_1, A_2 = constants defined in *Eq 9*
a_1, a_2 = constants defined in *Eq 29*
b = constant defined in *Eq 28*
C = penetrant concentration
C_o = penetrant concentration at the polymer surface

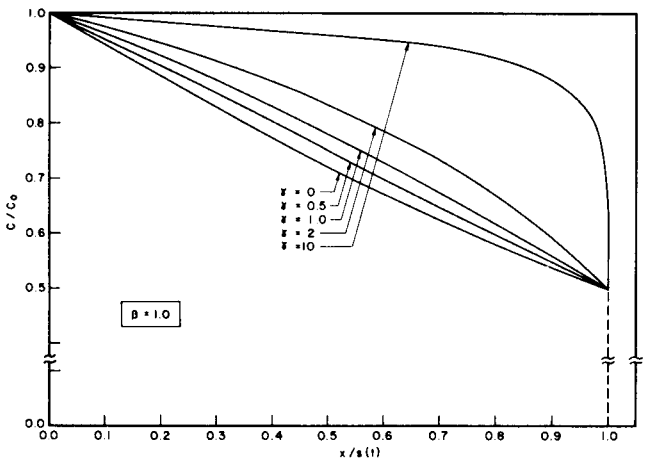

Fig. 2. Plot of computed values of C/C_o vs. $x/s(t)$ with γ as a parameter for $\beta = 1.0$.

Table 1. Comparison of Approximate and Exact Solutions for $\beta = 1$

x/s(t)	C/C$_o$ Approximate soln.	Exact soln.
0.0000	1.0000	1.0000
0.0863	0.9500	0.9513
0.1732	0.9000	0.9026
0.2615	0.8500	0.8536
0.3518	0.8000	0.8044
0.4450	0.7500	0.7549
0.5420	0.7000	0.7051
0.6442	0.6500	0.6546
0.7530	0.6000	0.6037
0.8706	0.5500	0.5522
1.0006	0.5000	0.5000

C_s = penetrant concentration at the moving boundary
D = diffusivity
D^* = dimensionless diffusivity, defined in *Eq 17*
D_s = diffusivity at the moving boundary
F = constant defined in *Eq 27*
h = function defined in *Eq 15*
k = constant defined in *Eq 12*
L = characteristic length of the polymer slab
s = position of the moving boundary
t = time
x = axial coordinate
β = constant defined in *Eq 25*
γ = constant defined in *Eq 31*
θ = dimensionless concentration, defined in *Eq 16*
ξ = dimensionless distance, defined in *Eq 19*
ξ_s = dimensionless distance, defined in *Eq 24*
τ = dimensionless time, defined in *Eq 18*

REFERENCES

1. N. L. Thomas and A. H. Windle, *Polymer*, **21**, 613 (1980).
2. H. L. Frisch, *Polym. Eng. Sci.*, **20**, 2 (1980).
3. A. Peterlin, *Polym. Eng. Sci.*, **20**, 238 (1980).
4. M. C. Hansen, *Polym. Eng. Sci.*, **20**, 252 (1980).
5. G. Astarita and G. C. Sarti, *Polym. Eng. Sci.*, **18**, 388 (1978).
6. J. Crank, "The Mathematics of Diffusion," 2nd Ed., Clarendon Press, Oxford (1975).
7. H. L. Frisch, T. T. Wang, and T. K. Kwei, *J. Polym. Sci.*, **A-2, 7**, 879 (1969).
8. L. F. Shampine, *Quart. J. Appl. Math.*, **30**, 441 (1973).
9. L. F. Shampine, *Quart. J. Appl. Math.*, **31**, 287 (1973).
10. W. F. Ames, *Ind. Eng. Chem. Fundam.*, **4**, 72 (1965).
11. P. Kehoe, *Chem. Eng. Sci.*, **27**, 1184 (1972).
12. B. Carnahan, H. A. Luther, and J. O. Wilkes, "Applied Numerical Methods," John Wiley, New York (1969).

fracturing the specimens. In the case of the specimens studied here, a craze density of approximately 250 cm^{-2} was obtained, with the craze length being approximately 0.1 mm.

The chromatography was carried out using a Waters GPC 201 with four microstyragel columns (10^6, 10^5, 10^4, and 10^3 Å), operating at a flow rate of 1.0 ml/min. Crazed and uncrazed specimens were dissolved in chloroform at 0.125 percent concentration, and the resulting chromatograms were converted to molecular weight distributions using calibrations obtained from nearly monodisperse polystyrene standards in the same solvent under identical flow rate and temperature conditions.

Preliminary studies had indicated that the difference in molecular weight averages for the crazed and uncrazed polystyrene specimens were small, and that the expected changes were on the same order (approximately 5 percent) as that inherent in the experimental procedure. To extract statistically significant information in the face of this limited precision and sensitivity, nine replications were performed for each of the crazed and uncrazed polystyrene specimens. (Each of the nine injections, however, was obtained from the same quantity of dissolved polymer; hence, it was the chromatography, and not the crazing and sampling procedure, which was replicated.)

RESULTS AND DISCUSSION

The computed values for the weight- and number-average molecular weight are shown in *Table 1*, along with the polydispersity $D = \overline{M}_w/\overline{M}_n$. Each of the nine chromatograms for the crazed and virgin specimens was converted to molecular weight distribution by a digitizer-computer system, and the resulting distributions were stored on disks from which they could later be recovered and manipulated. In particular, the computer could be asked to average the nine values of concentration at a given molecular weight so as to obtain an averaged overall distribution; the results of this curve averaging procedure are shown in *Fig. 1*. The two distributions in this figure have been normalized to represent the same total quantity of material. It is seen that crazing has produced a decrease in the concentration of the higher-molecular-weight species and an increase at the lower molecular weights, as would be expected from chain scission.

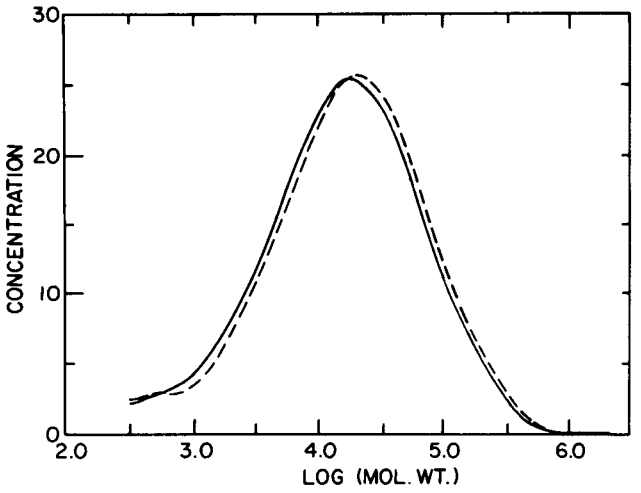

Fig. 1. GPC chromatograms for virgin and crazed polystyrene.

A cumulative distribution plot for the weight-average and number-average molecular weight $\overline{M}_w$ and $\overline{M}_n$ data from *Table 1* is plotted on a normal probability distribution scale in *Figs. 2* and *3*, respectively. *Figure 2* clearly shows a shift in $\overline{M}_w$ to lower values upon crazing. The effect of crazing on $\overline{M}_n$ is less clear, and this will be discussed below. Furthermore, a t-statistical test made on the $\overline{M}_w$ and $\overline{M}_n$ data indicates that one can state at 0.05 level of significance (assuming that $\overline{M}_w$ and $\overline{M}_n$ population are normally distributed) that the weight-average molecular weight has decreased upon crazing and fracture, whereas it is not possible to make a similar statement for the $\overline{M}_n$ due to the higher statistical variation in the $\overline{M}_n$ values.

These observations can be explained on the basis of the covalent bond scission. It is reasonable that the higher-molecular-weight, longer molecules rupture more often than the small ones. Longer chains, for instance, would be expected to contain more entanglements, which could lead to scission under stress. Therefore, the covalent bond rupture would affect the weight-average molecular weight more than the number-average molecular weight. Secondly, the polystyrene used for the analysis had a low-molecular-weight component (probably processing aids in this

Table 1. Molecular Weight and Dispersity Data for Virgin and Crazed Polystyrene

Virgin Polystyrene			Crazed Polystyrene		
Weight-Average Molecular Weight · 10^4	Number-Average Molecular Weight · 10^3	Dispersity	Weight-Average Molecular Weight · 10^4	Number-Average Molecular Weight · 10^3	Dispersity
3.402	4.369	7.8	3.081	3.465	8.9
3.630	4.773	7.6	3.192	5.902	5.4
3.633	4.330	8.4	3.403	4.045	8.4
3.909	4.865	8.0	3.483	4.091	8.5
4.026	5.885	6.8	3.611	4.829	7.5
4.135	5.069	8.2	3.760	6.580	5.7
4.226	6.192	6.8	3.921	6.674	5.9
4.315	7.198	6.0	4.083	6.640	6.1
4.402	7.141	6.2	4.260	7.439	5.7

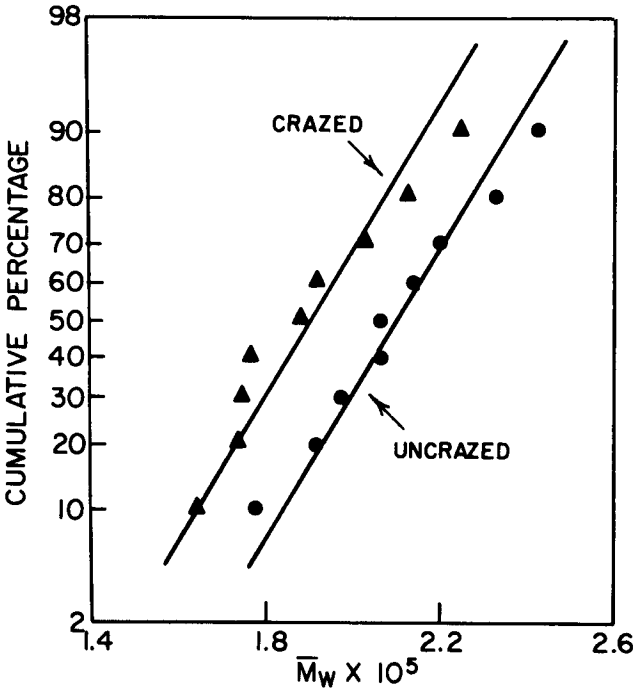

Fig. 2. Cumulative probability plot for weight-average molecular weights.

commercial material). This interferes with precise measurement of the concentration of the low-molecular-weight component of the polystyrene. Such an error will affect the number-average molecular weight more severely, and this may be one reason for the high statistical coefficient of variation (~20 percent) in $\bar{M}_n$ values.

It is our opinion that the numerical values for chain scission obtained from the chromatographic analyses are reliable and clearly show that substantial scission does accompany crazing. However, these experiments must be considered preliminary in many respects, and caution must be exercised before applying the numerical results to a detailed micromechanical analysis of the craze region. The uncontrolled nature of the manual stressing, with its uncertain stress states and the possibility of contamination with skin oil, is a problem that

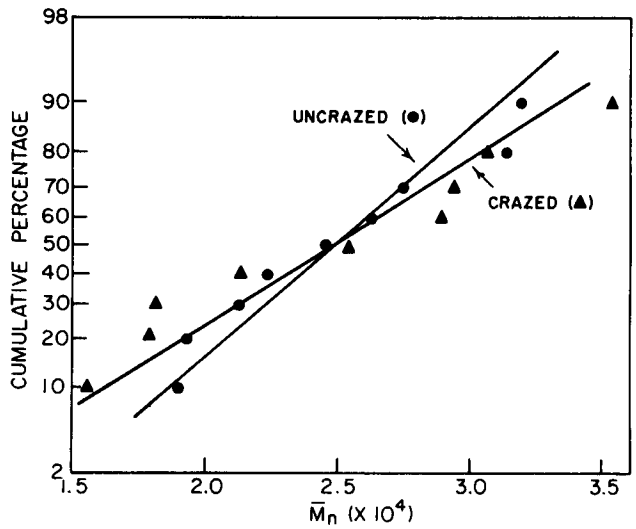

Fig. 3. Cumulative probability plots for number-average molecular weights.

future experiments should avoid. More serious, however, is the means by which craze density was computed here. This was done by manual counting in a transmission optical microscope but without taking pains to insure that all crazes were detected. As such, the quoted figure of 250/cm^2 of view for craze density may provide only a lower bound on the actual value. We expect that the craze density may, in fact, be substantially higher than this, since otherwise the observed chain scission values lead to an estimate for damage within the craze region that is unreasonably large. Since it is the degree of chain scission per unit of craze volume that is of principal interest, the craze volume must be measured with greater precision.

REFERENCES

1. R. P. Kambour, *J. Polym. Sci.: Macromolec. Rev.*, **7**, 1 (1973).
2. S. S. Sternstein and L. Ongchin, *Polym. Preprints, Am. Chem. Soc., Div. Polym. Chem.*, **10**, 1117 (1969).
3. A. S. Argon, *Pure Appl. Chem.*, **43**, 247 (1975).
4. D. K. Roylance, "Applications of Polymer Spectroscopy," p. 207, Academic Press (1978).