FINAL REPORT

"ENVIRONMENTAL STRESS CRACKING OF POLYMERS"

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ABSTRACT

A two point bending method for use in studying the environmental stress cracking and crazing phenomena is described and demonstrated for a variety of polymer/solvent systems. Critical strain values obtained from these curves are reported for various polymer/solvent systems including a considerable number of systems for which critical strain values have not been previously reported. Polymers studied using this technique include polycarbonate (PC), ABS, high impact styrene (HIS), polyphenylene oxide (PPO), and polymethyl methacrylate (PMMA). Critical strain values obtained using this method compared favorably with available existing data.

The major advantage of the technique is the ability to obtain time vs. strain curves over a short period of time. This allows, in most cases, sensitive determination of the nature of the transition between the time independent portion and the time dependent portion of the time vs. strain curve. The data obtained suggests that over a short period of time the transition in most of the polymer solvent systems is more gradual than previously believed.

Studies of the temperature effects in the PC/MIBK, PC/Cyclohexanone, and PPO/MIBK systems give results consistent with previous studies that support a plasticization mechanism for environmental stress cracking and crazing.

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1. INTRODUCTION.

Environmental stress cracking and crazing as initiated by liquid solvents has been described as the "Achilles heel" of glassy polymers because of the drastic reduction in strength associated with these phenomena. Mechanisms suggested to explain the role of liquids in these phenomena include surface stabilization, plasticization, and bond breaking; however, calculations made by Kambour[1] appear to rule out bond breaking as being a significant contributor to this process. In studying these phenomena, data are frequently obtained from experiments in which the time to crack or craze is measured as a function of decreasing stress. Curves produced from these data feature a vertical segment at higher stresses where the time to crack or craze is virtually instantaneous and a horizontal segment where the time to crack or craze is a function of stress. The critical stress (σ_c) is defined as the minimum stress that will produce crazing or cracking in the polymer/liquid system and can be determined reasonably by finding the point of intersection of the best lines drawn between the horizontal and vertical portions of the curve.[2,3]

Most studies have not obtained definitive data in the stress regions of the curves where the transition between the horizontal and vertical occurs. MacNulty[2,3] observed that in many cases this transition was much more gradual than previously believed, which opens to question whether the phenomena of environmental stress cracking and crazing are truly "critical" phenomena or if the transition between the horizontal and vertical portions of the curve represent some change in mechanism. Before this question can be answered a method must be developed that can produce the definitive data needed in the transition regions of these curves.

One of the most popular methods for obtaining the critical stress or strain parameter in environmental stress cracking and crazing was introduced by Ziegler[4] and improved by Bergen[5]. It does not in most cases involve direct measurement of time vs. stress or strain. This method uses a bending jig cut to defined elliptical or parabolic curves to which specimens are attached to the jig by means of side band clamps. The jig and specimen are then immersed in the solvent. In some cases wicks have been used to carry the solvent over the center of the specimen in order to avoid cracking along defect laden edges[6,7]. The specimen is kept immersed in the solvent for a period of time longer than is required for all cracking and crazing to cease. The specimen is then removed, and the critical strain is calculated from a knowledge of the geometry and the point at which the cracking or crazing stopped.

MacNulty[2,3] pointed out a number of weaknesses in this technique. The most serious of these is that it is impossible to obtain short time readings for the immersion of samples, since the time required for draining and drying the specimen is in many cases on the same order of magnitude as, or longer than, the immersion itself. Furthermore, one of the greatest experimental difficulties is detecting exactly where cracking stops, particularly in opaque or fogged samples. Another difficulty cited by MacNulty[2,3] is the possibility that the specimen may lift off the jig if it is not clamped with side bands. This may affect the strain in an undetermined manner.

Some studies have been made by applying straight tension to the samples, first qualitatively by MacNulty[8] using heat treated films. Bergen[9] introduced a technique in which a constant creep load is placed on the specimen and the time to break measured as the time at which the environmental creep curve deviates sharply upward, since one or more of the mechanical properties of the polymer will change abruptly at the outset of cracking. MacNulty[2,3] used tensile tests successfully in measuring time to break vs. load for solvent applied to the surface of standard dumbbell tensile test specimens. This procedure yields reasonably good time to break vs. load curves from which the critical strain can be determined. Bernier and Kambour[10] used a three-point loading technique successfully with polyphenylene oxide (PPO); however, readings in these experiments were taken after relatively long periods of time. Henry[11] introduced a novel technique that utilizes a three-point loading technique in which a transducer senses a change in force when the sample is immersed in solvent.

It was our feeling that more information could be obtained on the phenomena of environmental stress cracking and crazing if a simple method could be developed for studying short term effects. If time to crack or craze curves could be generated over short periods of time and wide ranges of strain using numerous replicate samples, more precise curves could be obtained. Of particular value would be information on the regions of transition between the vertical and horizontal sections of the time vs. strain curves. For this purpose we have developed a method using a simple two-point loading technique that allows the processing of a relatively large number of specimens and thus data points over a short period of time.

Studies of the temperature effects on the environmental stress cracking and crazing of polymers have been performed principally by Andrews and Bevans[12], and Earl, Loneragan, Jones, and Crook[13] on polystyrene and polymethylmethacrylate (PMMA) and to a limited extent MacNulty[3] working with polycarbonate (PC), polyphenylene oxide (PPO) and other polymers. Andrews and Bevans[12] showed that in polystyrene/alcohol and PMMA/alcohol systems the estimated minimum surface work (F_0) required to propagate cracking or crazing decreased with temperature until the same temperature (T_c) was reached, at which time F_0 became constant. Earl, et al.[13] using polystyrene and PMMA specimens mounted on elliptical jigs and immersed in various alcohols found that the critical strain for cracking decreased through a narrow temperature range of about 30°C. The critical strain (ε_c) was found to be constant both above and below this temperature range. A second characteristic temperature, T_s, in addition to T_c, was associated with their data. T_s was defined as the midpoint of a 30°C range of temperatures where the critical strain decreases. This behavior was attributed to a glass-rubber transition in the polymer due to the plasticization resulting from the equilibrium sorption of solvent occurring in the temperature region corresponding to the range of temperatures where the decrease in crazing strain was observed. This behavior was attributed to the plasticizing effect of the solvent. MacNulty[3] argues that plots of F_0 vs. T and ε_c vs. T should have the same form if there is a critical crack length. MacNulty[3] did not observe any temperature variation of ε_c in tests above room temperature with PC, PPO, and polysulphone. These results were attributed to the fact that T_c must lie somewhere below room temperature for the systems studied.

In other studies, Kambour, et al. showed that the critical strain (ε_c) decreased as the glass transition temperature (T_g) decreased with increasing solvent concentration in polystyrene[7,14], PPO[14], polysulfone[14] and PC[14] swelled to various degrees in solvent or as in the case of polystyrene preplasticized with various fractions of o-dichlorobenzene.

In the work reported in this paper, studies have been made of the variation of ε_c in PC/cyclohexanone and PC/methylisobutyl ketone (MIBK) systems and the PPO/MIBK system to show that T_c and T_s can be found below room temperature as predicted by MacNulty[3] and to relate a T_s to a corresponding T_g for each system studied.

2. EXPERIMENTAL.

2.1 Test Specimens.

Test speciments of 15 mm width and 150-180 mm length were cut from commercially obtained sheets of various materials. Specimens from the transparent materials were shown by bifringence patterns to be nearly free of strain.

2.2 Materials.

Polymers - Good quality commercial sheets were used in all cases, except in the cases in which sheets were compression molded from the resin:

ABS - S. S. Plastics, Denver, CO.

Cellulose Acetate - Franklin Fibre-Laminex Corporation, Lake Success, New York.

High Impact Styrene - Franklin Fibre-Laminex Corporation, Lake Success, New York.

Nylon 6/6 - S. S. Plastics, Denver, CO.

Polybutylene Terephtalate - GE Valox Resin (compression molded sheet).

Polycarbonate - Rohm and Haas "Tuffax" Sheet, GE Lexan PC Sheet, S.S. Packaging, Denver, CO.

Polymethyl Methacrylate - Rohm and Haas "Pexiglass G" Sheet, S. S. Packaging, Denver, CO.

Polyphenylene Oxide - GE Noryl 1000 sheet.

Polyphenylene Sulfide - Phillips "Ryton" PPS (compression molded sheets).

Solvents - High quality Reagent or C.P. grade solvents were used in all cases.

2.3 Experimental Procedure.

The final sample configuration (Fig. 1) was obtained using a two-point loading technique. In this technique the specimens were bent by applying pressure to the ends of the strips. The strips were then held in this position by the jig. Solvent was then applied dropwise with a stirring rod to the upper surface (tension) of the specimen at the apex of the bend, taking care not to touch the surface of the specimen with the stirring rod itself. Close attention was paid to avoid the edges of the specimen with the solvent, since cracks initiated at the edges of the strips are much more rapid than otherwise. Craze and/or crack formation was then observed in the specimen with the naked eye or with a 4 or 8 diopter magnifier.

In the preliminary qualitative tests, the strips were placed under relatively high strain (>.02) and tested for a tendency for rapid environmental stress cracking or crazing (Table I). In these tests if cracks or crazes were not observed in five minutes, the plastic was not considered susceptible to rapid environmental stress cracking. In the quantitative tests the time to crack or craze was measured as the time required for the first visible crack or craze to appear under the viewing conditions. The best viewing conditions varied from material to material; thus many preliminary runs were performed to find the optimum conditions of light angle (usually oblique and horizontal to the sample), magnification, etc. Cracking and crazing were much more difficult to observe in the opaque polymers as compared to the transparent polymers. Using these techniques, times to crack or craze were determined as a function of strain by varying the span of the jig and thus the curvature of the sample.

2.4 Calculation of Strain.

The two-point loading technique is accomplished by applying buckling loads at the ends of the specimen strips. The final configuration is diagramed in Figure 1. The moment at point A is M = -Wv, where W is the load and v is the deflection at X. Williams[15] has analyzed this configuration for the small and large deflection cases. For the case where the deflections are not large we may write:

$$\frac{1}{R} = \frac{d^2v}{dx^2} \Big/ \left[1 + \left(\frac{dv}{dx}\right)^2 \right]^{3/2} = \frac{d^2v}{dx^2} = \frac{M}{EI} = \frac{-W_v}{EI} \quad \text{(Williams }^{15}\text{).}$$

This differential equation gives the solution $v = C_1 \sin\left(\sqrt{\frac{W}{EI}}\right)x + C_2 \cos\left(\sqrt{\frac{W}{EI}}\right)x$; x=0,v=0 and v=0, x=ℓ give boundary conditions such that $C_2=0$ and $0=C_1\sin\sqrt{\frac{W}{EI}}\,\ell$. The second condition can be met for any value of C_1 if $\sqrt{\frac{W}{EI}}\,\ell = n\Pi$ where n=0, 1, 2, 3, ... The shape of the curve is given by $v = C_1\sin\left(\sqrt{\frac{W}{EI}}\right)x = C_1\sin\left(\frac{n\Pi\ell}{\ell}\right)$. For a full sine wave as indicated in Fig. 1, n=1. At the maximum deflection $v = v_{max}$, $x=\ell/2$. Then $v_{max} = C_1\sin\left(\frac{\ell/2}{\ell}\right)\Pi = C_1\sin \Pi/2$, thus $C_1 = \frac{v_{max}}{\sin \Pi/2} = v_{max}$.

The relevant derivatives are given by:

$$\frac{dv}{dx} = \frac{\Pi\, v_{max}}{\ell} \cos \frac{\Pi x}{\ell}$$

$$\frac{d^2v}{dx^2} = -\frac{\Pi^2 v_{max}}{\ell^2} \sin \frac{\Pi x}{\ell}$$

At $v = v_{max}$

$$\frac{dv}{dx} = \frac{\Pi\, v_{max}}{\ell} \cos \frac{\Pi}{2} = 0$$

$$\frac{d^2v}{dx^2} = -\frac{\Pi^2 v_{max}}{\ell^2} \sin \frac{\Pi}{2} = \frac{-\Pi^2 v_{max}}{\ell^2}$$

Since $\varepsilon = \frac{d}{2R}$ (Bergen, 1962), $\varepsilon = \frac{\Pi^2 v_{max} d}{2\ell^2}$ (1) which is valid for the small deflection case. It can also be shown that $WL^2/EI = \Pi^2$[15]. In extending this case to the large deflection case we do not have to be concerned with the discrepancy that $1/R = d^2v/dx^2 \Big/ \left[1 + \left(\frac{dv}{dx}\right)^2\right]^{3/2}$ since at $v = v_{max}$ $dv/dx = 0$. Thus $1/R = \frac{d^2v}{dx^2}$ at all deflections if we assume the curve retains the basic sine curve shape. However, in consideration of the large deflection case, Williams[15] shows that $\frac{WL^2}{EI} = 4K^2$ where K is the elliptical integral

$$K = \int_0^{\pi/2} \frac{d\gamma}{\sqrt{1 - \sin^2(\alpha/2)\sin^2\gamma}}$$

$$= \pi/2 \left[1 + 1/4 \sin^2 \alpha/2 + 9/64 \sin^4 \alpha/2 + \frac{225}{2304} \sin^6 \alpha/2 + \ldots +\right] (2).$$

If in the small deflection case

$$\pi^2 = \frac{WL^2}{EI} \text{ and } (1),\ \varepsilon = \frac{\pi^2 v_{max} d}{\ell^2}.$$ Then

$$\varepsilon = \frac{(WL^2/EI)v_{max}d}{\ell^2}.$$ We can then correct for large deflections by substituting

$4K^2 = WL^2/EI$ giving

$$\varepsilon = \frac{4K^2 v_{max} d}{2\ell^2} = \frac{2K^2 v_{max} d}{\ell^2} \quad (3).$$

This correction is valid only within the elastic limit.

The elliptical integral is a function of the angle $\alpha/2$ which in these experiments is not accurately determinable. However, Williams[15] shows that

$$-v_{max}/L = \frac{+\sin \alpha/2}{K} \quad \text{or} \quad -\frac{L}{v_{max}} = \frac{K}{\sin \alpha/2}$$

$$= \pi/2 \left[1 + 1/4 \sin^2 \alpha/2 + 9/69 \sin^4 \alpha/2 + 225/2304 \sin^6 \alpha/2 + \ldots + \right] / \sin \alpha/2$$

$$= \pi/2 \left[\sin^{-1} \alpha/2 = 1/4 \sin \alpha/2 + 9/64 \sin^3 \alpha/2 + 225/2304 \sin^5 \alpha/2 + \ldots + \right].$$

A plot of this function vs. $-L/v_{max}$ indicates that a power curve of the form $-L/v_{max} = a(\text{arc cosec}^b\ \alpha/2)$ may provide a reasonable fit. Regression analysis of calculated values of L/v_{max} calculated from arbitrary values of $\alpha/2$ and corresponding K value obtained from math tables give a = 1.7343197 and b = .9590071 with a correlation coefficient of $r^2 = .9983$. From these parameters $\sin \alpha/2$ can be calculated:

$$\sin \alpha/2 = \left(\frac{-1.7343197 v_{max}}{L} \right)^{1/.9590071}$$

K can then be calculated from sin α/2 and equation (2); then E may be calculated from equation (3). Stress may then be calculated from a knowledge of Young's modulus (E); $\sigma = \varepsilon E$. The data were processed with the aid of a Tektonix 4051 minicomputer system.

2.5 Temperature Control.

All specimens were run at ambient room termperature (24-26^{o}C) except for those systems in which the critical strain was determined as a function of temperature. In these systems temperature was controlled within a range of about -10^{o}C to 50^{o}C using intervals of approximately 5^{o}C using the air baths pictured in Figures 2 and 3 controlled by a YSI Model 71A temperature controller and air probes. For temperatures above ambient room temperature, a modified incubator was used (Fig. 2), and for temperatures below ambient room temperature a 6 cu. ft. freezer was used (Fig. 3). In each case the units were modified to accommodate the external YSI controller and probes. It was necessary to modify the openings of the containers to allow visual and physical access to the specimens inside the bath. This was accomplished by building a sliding window of polycarbonate with a small hole (3 cm. diameter) in the middle. Temperature control for the samples was maintained in the range ± 0.5^{o}C in both the hot and cold bath. Time to crack or craze could then be determined as previously described.

The effect of cooling the specimen as a result of evaporation of the solvent from the surface was measured by attaching a thermistor probe to the surface of some specimens. The temperature drop as a result of evaporation was then followed for a number of solvents at various bath temperatures. From the results it was found that the experiment would have to be limited to solvent cracking agents of relatively low volatility. The volatilities of cyclohexanone and MIBK were low enough to maintain temperature control within the limits of $\pm$ 0.5°C over the temperature range studied.

2.6 Specimens for T_g Determination.

Weighed strips of polycarbonate were plasticized at 160 - 170°C in a Plasticord machine. Once flow was established, cyclohexanone was added. After mixing to assure homogeneity, the plasticized PC/cyclohexanone blend was weighed, and the percent cyclohexanone was calculated. A weighed portion of this blend was then compression molded into sheets and then weighed again to determine solvent losses, and the percent cyclohexanone was then recalculated. A small sample was then punched from the sheet and T_g determined by thermal analysis using a Perkin-Elmer DSC II.

The same procedure was attempted for producing PC/MIBK blends. Unfortunately, MIBK proved too volatile at the elevated temperatures to obtain more than a few percent MIBK, and in some cases a reaction occurred that completely changed the properties of the polymer. Therefore, specimens of varying gross compositions of MIBK were prepared by swelling weighed polycarbonate strips in MIBK for varying periods of time. After allowing the surface of the strips to dry, the strips were reweighed and the percent MIBK calculated from the weight increase. T_g was then determined by thermal analysis as in the case of PC/cyclohexanone.

In cases where thermal analysis could not be performed immediately, the specimens were sealed in polyethylene bags to reduce solvent evaporation.

3. RESULTS.

3.1 Critical Strains from Two-Point Bending Method.

Figures 4-8 are representative curves obtained from plots of strain versus time obtained using the two-point loading technique. Plots of strain versus time for additional systems are given in Appendix I. Values for the critical strain were obtained by the linear extrapolation of the vertical and horizontal segments of the curve to the point of intersection, ignoring points in the transition region of the curve. A linear regression analysis was used in most cases to fit points on the horizontal portion of the curve. Tables II and III list critical strain values obtained in this manner for various polymer/solvent systems. The uncertainties in Tables II and III represent the standard deviation for the points of intersection of the horizontal and vertical lines, and as such they should be viewed as the minimum uncertainties. Where possible these values are compared to the tensile and bending experiments of MacNulty[2,3]. Reasonable comparisons are obtained in most cases, particularly when compared to the bending experiments. Where comparisons are not good, it should be noted that the two-point technique generally yields higher values. In this work we made the observation consistent with MacNulty[2] that the curves exhibited three basic types of behavior:

1) Systems that cracked or crazed in less than a second at stresses above the critical stress or did so only after a relatively long period of time.
2) Systems similar in behavior to the systems in 1) but with ranges of stress where almost any value for the time to break occurred.
3) Systems in which there was a smooth transition from a rapid time to break to a long time to break.

The type behavior (1, 2, 3) observed for each system is indicated in Tables II and III.

In most systems studied it can be seen from Tables II and III that smooth transitions were observed between the time independent and time dependent portions of the curves. It should be noted, however, that variations in the sharpness of breaks did occur. This can be readily seen by comparing, for example, the curve in Fig. 7 with the curve in Fig. 8. All of these curves show a gradual transition, but the transition in Fig. 8 is much sharper than the others.

Another observation made was the fact that the relative scatter of points varied considerably from one system to another. This scatter can be traced directly to observational problems. In many cases the scatter of points for a particular curve appears to be a function of the relative opacity of the sample. In Figs. 4 and 5 very little scattering of points is observed with transparent polycarbonate, whereas the scatter of points in Figs. 6 and 7 is much greater with the opaque ABS and HIS. This scatter can be attributed to the increased difficulty an observer has in discerning when cracking or crazing has commenced. Some opaque systems were easier to work with than others as evidenced by Fig. 8., the PPO/MIBK system. Another problem was that in some cases very fine networks of horizontal crazing were produced which made it difficult for the observer to determine the time required for the outset of crazing precisely.

It should be noted that a major difference between our experiments and MacNulty's is that we measured the time required to observe the first indication of cracking or crazing whereas MacNulty measured the time to break. Although in some cases the values for the critical strain and stress appear to be somewhat higher than those of MacNulty, the general behavior observed is consistent. Bergen[9] showed that the time to break is about 10 times as long as the time to crack. Our technique also allowed many more data points in the transition region of the curves to be obtained. The combination of these factors results in the production of curves that run over a range of times much shorter than MacNulty's[2,3] with many more points in the transition region. In drawing the lines that form the horizontal portion of the curve, we thus have a better feel for where the transition portion of the curve ends, which should give us a more sensitive measure of the critical strain, but this also generates lines of somewhat greater negative slope, resulting in higher extrapolated values for the critical strain.

Many additional systems other than these reported in Tables II and III were studied qualitatively and found to be unsuitable for study using the two-point technique because the times required for cracking were exceedingly long.

3.2 Temperature Effects.

Figures 9, 10, and 11 are plots of ε_c vs. T for PC/cyclohexanone, PC/MIBK, and PPO/MIBK. Although there is a considerable degree of scatter in the points, the trend observed in the three curves is consistent with the data of Andrews and Bevans[12] and Earl, et al.[13] for PMMA and polystyrene in alcohols, assuming, of course, that the F_0 vs. T curves and ε_c vs. T curves have the same form. Table IV gives values for T_c and T_s estimated from the curves. T_c values approximated from the curves are 10-20^oC for PC/cyclohexanone, about 12^oC PC/MIBK and about 22^oC for PPO/MIBK. T_s was more difficult to approximate, since in the case of PPO/MIBK and to some extent PC/cyclohexanone, the leveling of ε_c occurred at some temperature lower than -10^oC which was the limit of our system. However, in the polycarbonate system, values for T_s are estimated at -5 - +5^oC for PC/cyclohexanone and about 8^oC for PC/MIBK. Using an approximate range of 30^oC as in the case of Earl, et al.[13] one derives a value for T_s of about 0-5^oC for the PPO/MIBK system.

As predicted by MacNulty[3], these values, although approximate, all lie below room temperature for PPO and polycarbonate for the solvents tested.

Figures 12-14 are strain vs. time curves plotted from PC/cyclohexanone data at three different temperatures: 0^oC, 25^oC, and 50^oC. These figures illustrate typical curves obtained when the times to form discontinuities are plotted as a function of strain. All three curves are similar in that they have the characteristic vertical and horizontal portions. In the vertical portions, the time to form a discontinuity is virtually instantaneous, while in the horizontal portions, the time to form a discontinuity is time dependent. In between these two characteristic portions of the curve lies a region where there is a transition between the vertical and horizontal portions of the curve. The major change observed in the curves other than that they yield different values for ε_c is the observation that the transition region of the curve is shortened dramatically with increasing temperature. At $0^{o}C$ the transition region of the curve ends on the order of magnitude of hundreds of seconds. At $25^{o}C$ this time is shortened to the order of magnitude of tens of seconds, and at $50^{o}C$ it is shortened further to the order of magnitude of a few seconds. Also note the relative decrease in the scatter of points around the transition region with increasing temperature. A complete set of curves for all the systems and temperatures appear in Appendix 1. The observation of Earl, et al.[13] that the time for the last craze to form decreased with increasing temperature is consistent with this observation and can be attributed to an increase in the rate of stress relaxation.

Another interesting observation was an apparent change in the morphology of the discontinuities with increasing temperature which was observable in polycarbonate. At strain above ε_c where discontinuities appeared virtually instantaneously, it was observed that at the lowest temperatures the discontinuities appeared as cracks, sometimes breaking the specimens in two, while at the higher temperatures, the discontinuities appeared as a network of very fine crazes normal to the stress. Earl, et al.[13] argues that T_s corresponds to a glass-rubber transition within a small plasticized volume of polymer in which the craze initiates. Evidence for this hypothesis was obtained by measuring T_g in a series of specimens of polystyrene and PMMA equilibrated with various solvents. T_g was then compared with T_s. The T_g's obtained from the equilibrated specimens yielded values higher than corresponding values of T_s, but higher by approximately constant differences [13]. Kambour, et al.[7,14] showed that the critical strain for crazing in polystyrene, PPO, polysulfone and polycarbonate decreased with increasing solvent concentration and a corresponding decreasing T_g. A decreasing resistance to crazing with increasing plasticization was shown to occur up to some optimum solvent concentration at which point the specimens became so rubbery that the crazes healed themselves as they formed[4].

In this work an attempt was made to determine T_g as a function of solvent concentration in a manner similar to Earl, et al.[13] and Kambour, et al.[7,14] but with somewhat limited success. In both cases, as can be seen in Figure 7, T_g is as expected depressed as a function of solvent concentration. The best results were obtained in the PC/cyclohexanone system where the polymer was plasticized directly. Erratic behavior of the DSC II made the determination of accurate T_g values difficult, resulting in the scatter of points observed in Figure 7. It is possible that evaporation of solvent from the specimen during the scan or heterogeneities in the sample were the source of this problem. Applying the Kelly-Bueche[16] equation using the same assumptions as Kambour, et al.[14] for polycarbonate yields a curve that for the most part falls below our experimental points. By extrapolation of the theoretical Kelly-Bueche[16] curve in Figure 15 to temperatures corresponding to the T_s values derived from the critical strain/temperature curves, one obtains what might be referred to as a "critical" solvent concentration, which is the fraction of solvent required to lower T_g to a value corresponding to T_s. In the case of polycarbonate, that would be at a solvent fraction in the range of 30 volume percent. This data would seem to be consistent with the plasticization hypothesis and suggests that in the crazing process at or below the critical strain the fraction of solvent in the system must increase to some optimum value before crazing occurs.

4. CONCLUSION.

In this study we have developed a new test method that appears to be satisfactory for determining the critical stress and strain parameters for polymeric materials with various liquid ESCC agents. The method appears to be most effective when used with transparent polymers. The method allows much more data in the transition region between the horizontal and vertical regions of the curves than any previous method. In addition to obtaining critical strain values comparable to those obtained by other methods, many critical strain values have been obtained for polymer/solvent systems not heretofore reported. Data obtained using the two-point method indicates that the transition from the instantaneous to finite portions of the curve is much more gradual than previously believed. MacNulty[3] suggested that the vertical portion of the curves obtained in ESCC represent a true stress cracking behavior which is effectively instantaneous, whereas the horizontal portion of the curve is slower and may be controlled by a different mechanism. If this is true, the critical stress or strain is the stress or strain at which this second mechanism becomes predominant, and the transition region of the curve is the region where the two mechanisms compete with one another. Further evidence for competing mechanisms is given from the observation that at high strain (well above the critical strain) some polymers fracture instantaneously, but as the strain is reduced to values approaching the critical strain only fine networks of crazes are produced. The temperature effects observed are consistent with the plastization mechanism for crazing.

TABLE I.

SUMMARY OF PRELIMINARY STRESS CRACKING TESTS

	PC	PPS	CA	NYLON 6/6	ABS	PBT	CAB	HIS	PPO
Acetone	x	n	d	n	c	n	n	d	c
Benzene	c		n	n	c	n	c	d	c
2-Butanone	x	n	d	n	c	n	n	d	x
n-Butyl Bromide	x	n	n		c	n	n	d	c
CCl_4	x	n	n		n	n	n	d	d
$CHCl_3$	x	n	d		n	n	c	d	n
Cyclohexane	c	n	n		n	n	n	d	x
DMF	c	n	c	n	n	n	n	d	n
DMSO	c	n	n		n	n	n	c	n
Et. Acetate	x	n	d		c	n	n	d	c
2-Propanol	x		n		n	n	n	n	n
HCl (6M)	n	n	n	n	n	n	n	n	n
MIBK	x	n	n		d	n	c	d	c
Toluene	c	n	n		c	n	c	d	c
Xylene	x		n	n	n	n	c	d	n
Methanol	c	n	d		x	n	n	c	x
HNO_3(6M)	n	n	d		n	n	n	n	n
NaOH (6M)	n	n	d		n	n	n	n	n
1-Butanol	c		d		n	n	n	c	n
Glycerin	c		n		n	n	n	n	n
Hexane	c		n		n	n	c	n	n
Formic Acid	n		d	n	c	n	n	c	c
Con. NH_3	n		n	n	n	n	n	n	n
Cresol	c		c	n	n	n	n	n	n

TABLE I. Continued

	PC	PPS	CA	NYLON 6/6	ABS	PBT	CAB	HIS	PPO
Eth. Glycol	n		n		n	n	n	n	n
Cyclohexane	x		c		d	n	c	d	n
Diacetin	x		n		c	n	c	c	c
Methyl Acetate	c		d		d	n	d	d	c
Ethylene Dichloride	c		n		d	n	n	d	d

c - cracks or crazes

n - no apparent effect

d - dissolves

x - full complement of time to crack vs. strain data

PC - Polycarbonate

CA - Cellulose Acetate

CAB - Cellulose Acetate Butyrate

PPO - Polyphenylene Oxide

PPS - Polyphenylene Sulfide

PBT - Polybutylene Terephtalate

HIS - High Impact Styrene

TABLE II

CRITICAL STRAIN AND STRESS VALUES OBTAINED FOR POLYCARBONATE (PC) / SOLVENT SYSTEMS

Solvent	ε_c	σ_c(MPa)	σ_c(MPa)Lit[2,3]	Type Behavior
Acetone	.0037 ± .0001	8.3 ± .2	5.5 ± 1.4 (4.7)	3
Benzene	.0055 ± .0004	12.4 ± .9		3
2-Butanone	.0084 ± .0008	19 ± 2		3
CCl_4	.0059 ± .0004	13.3 ± .9	8.3 ± 1.4 (6.7)	1
$CHCl_3$	.0077 ± .0008	17 ± 2		3
Diacetin	.0170 ± .0007	38 ± 2		3
DMSO	.0077 ± .0007	17 ± 2		3
Ethyl Acetate	.0085 ± .002	19 ± 3	47.6 ± 2.7 (8.1)	1
Isopropanol	.028 ± .005	63 ± 11		3
MIBK	.0039 ± .0003	8.8 ± .7		3
n-Butyl Bromide	.0024 ± .0001	5.3 ± .2	5.5 ± 1.4 (7.4)	3
Xylene	.0039 ± .0001	8.8 ± .2	15.2 ± 4.1	3
Cyclohexanone	.0073 ± .0006	16 ± 1	6.9	3

TABLE III

CRITICAL STRAIN AND STRESS VALUES FOR ABS, CELLULOSE ACETATE BUTYRATE (CAB) AND HIGH IMPACT STYRENE (HIS)

Polymer/Solvent	ε_c	σ_c	σ_c(Lit)	Type Behav.
ABS/Acetone	.046 ± .008	37 ± 6		2
ABS/Benzene	.018 ± .003	14 ± 2		2
ABS/Diacetin	.010 ± .001	8.1 ± 8		3
ABS/Formic Acid	.0129 ± .0002	10.4 ± .2		3
ABS/Acetic Acid	.0043 ± .0003	3.5 ± .2		3
ABS/MIBK	.0043 ± .001	3.5 ± .8		3
ABS/n-Butyl Bromide	.017 ± .001	13 ± 1		2
CAB/Cyclohexanone	.016 ± .002			3
HIS/Acetic Acid	.0021 ± .0001	3.0 ± .1		1
HIS/Diacetin	.055 ± .010	80 ± 15		3
HIS/DMSO	.010 ± .001	14 ± 1		3
HIS/Formic Acid	.024 ± .004	35 ± 6		3
PPO/Cyclohexane	.0064 ± .0008	6.8 ± 8	7.5 ± .5	3
PPO/Methyl Acetate	.0028 ± .0003	3.0 ± .3	4.1 ± .8	3
PPO/2-Butanone	.0023 ± .0001	2.4 ± .1		3
PMMA/Acetone	.0029 ± .0001	8.5 ± .3		3
PMMA/Ethylene Dichloride	.0026 ± .0002	7.6 ± .6		3
PMMA/DMF	.0022 ± .0003	6.4 ± .9		3
PMMA/2-Butanone	.0029 ± .0001	8.5 ± .3		3

TABLE IV

Polymer/Solvent	T_c (^oC)	T_s (^oC)
PC/cyclohexanone	10-20	-5 - +5
PC/MIBK	~12	~8
PPO/MIBK	~22	0 - 5

FIGURE 1. SPECIMEN WITH END LOAD AND LARGE DEFLECTIONS

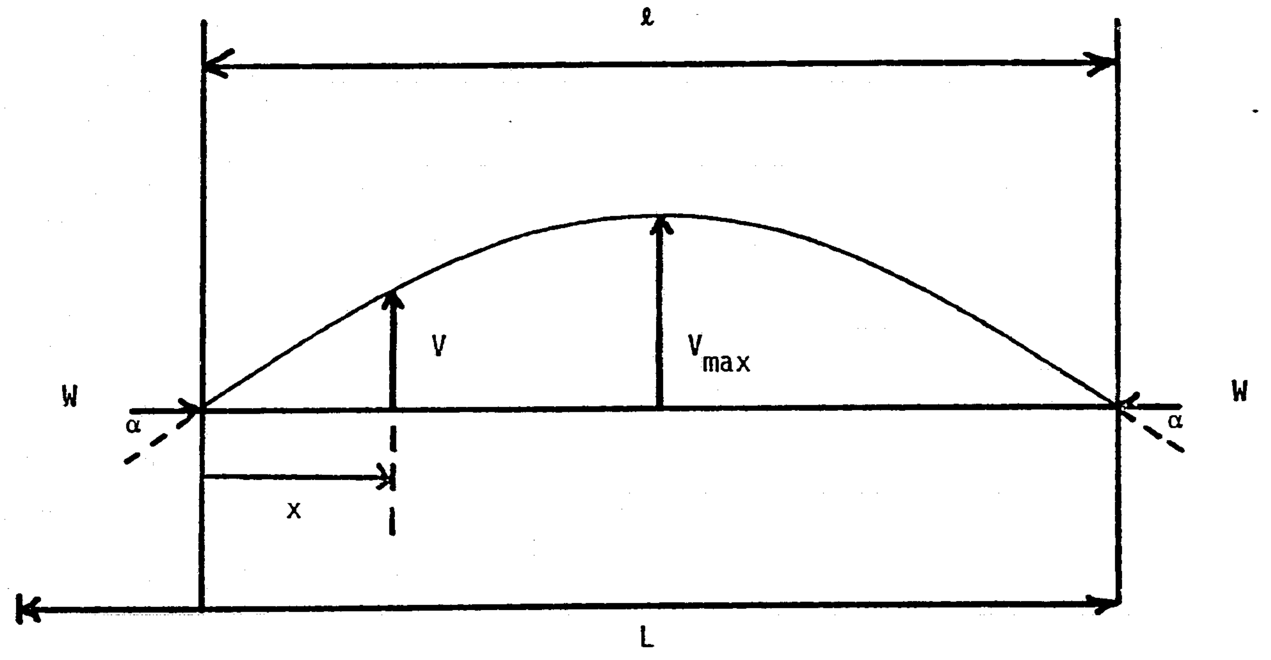


FIGURE 2. 'HIGH' TEMPERATURE AIR BATH

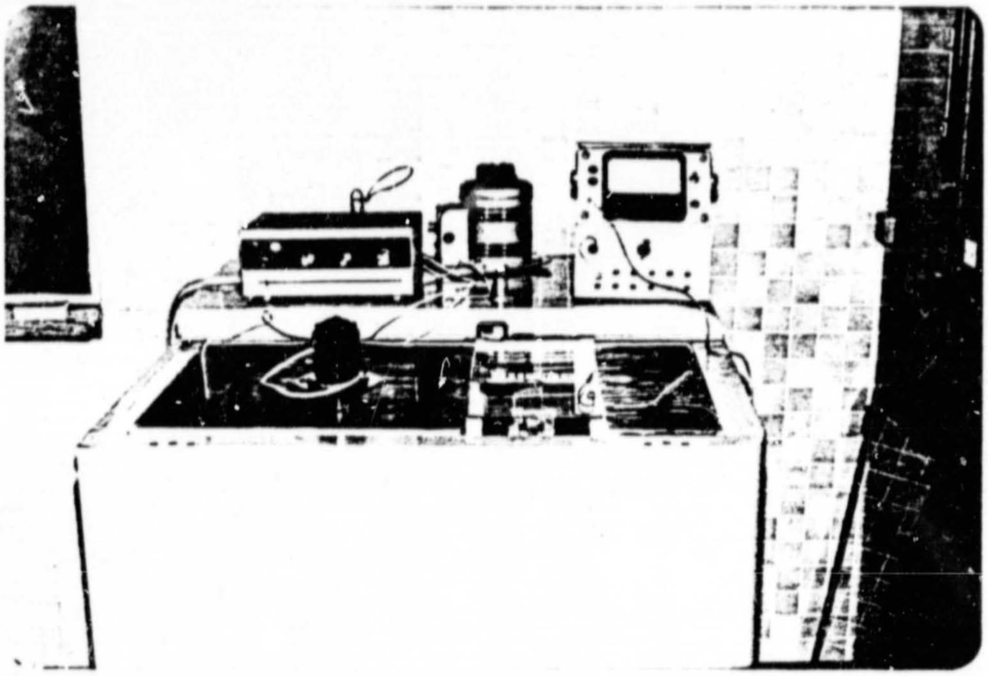


FIGURE 3. 'LOW' TEMPERATURE AIR BATH

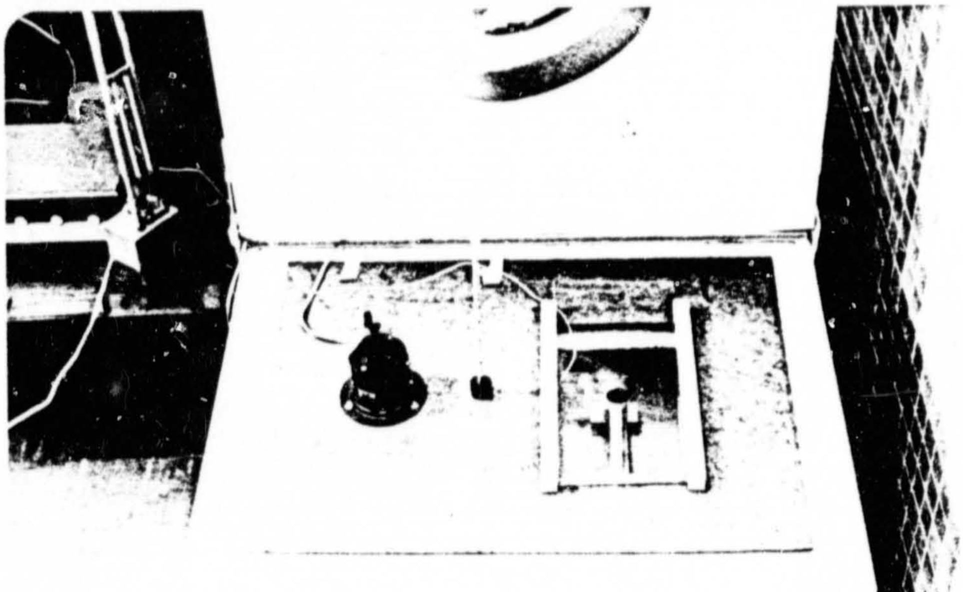


FIGURE 4. POLYCARBONATE/CHLOROFORM

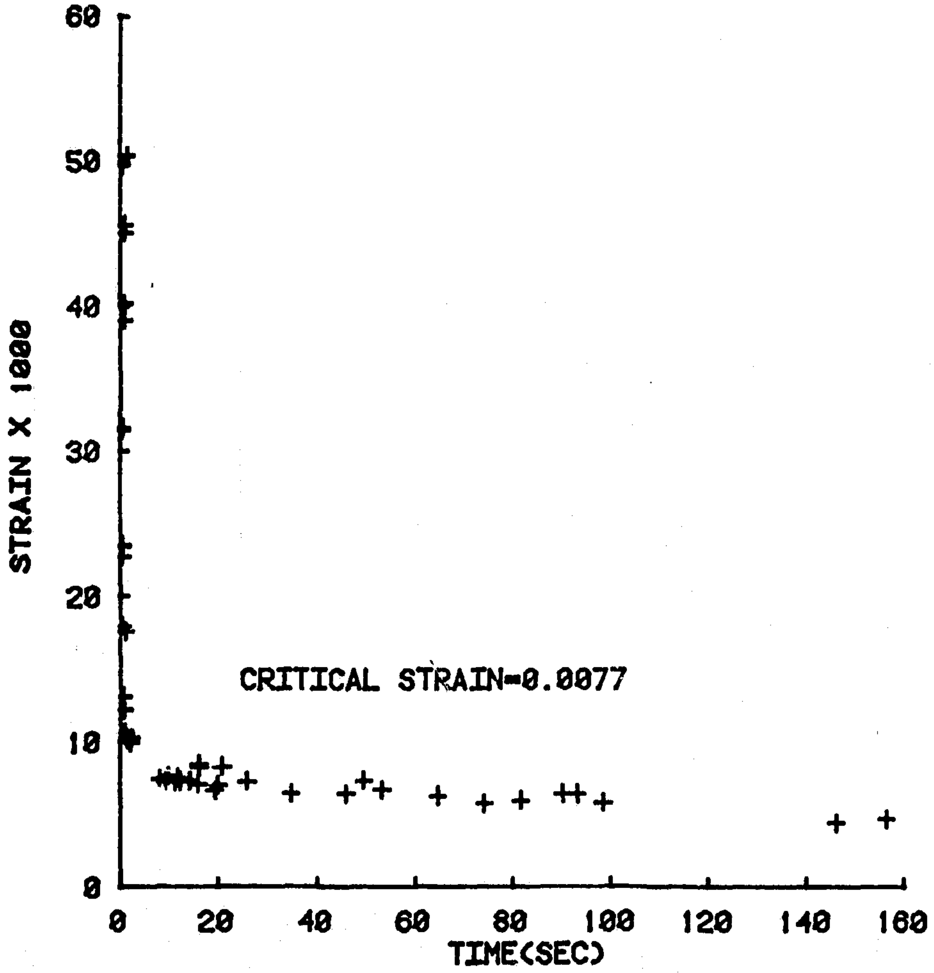


FIGURE 5. POLYCARBONATE/MIBK

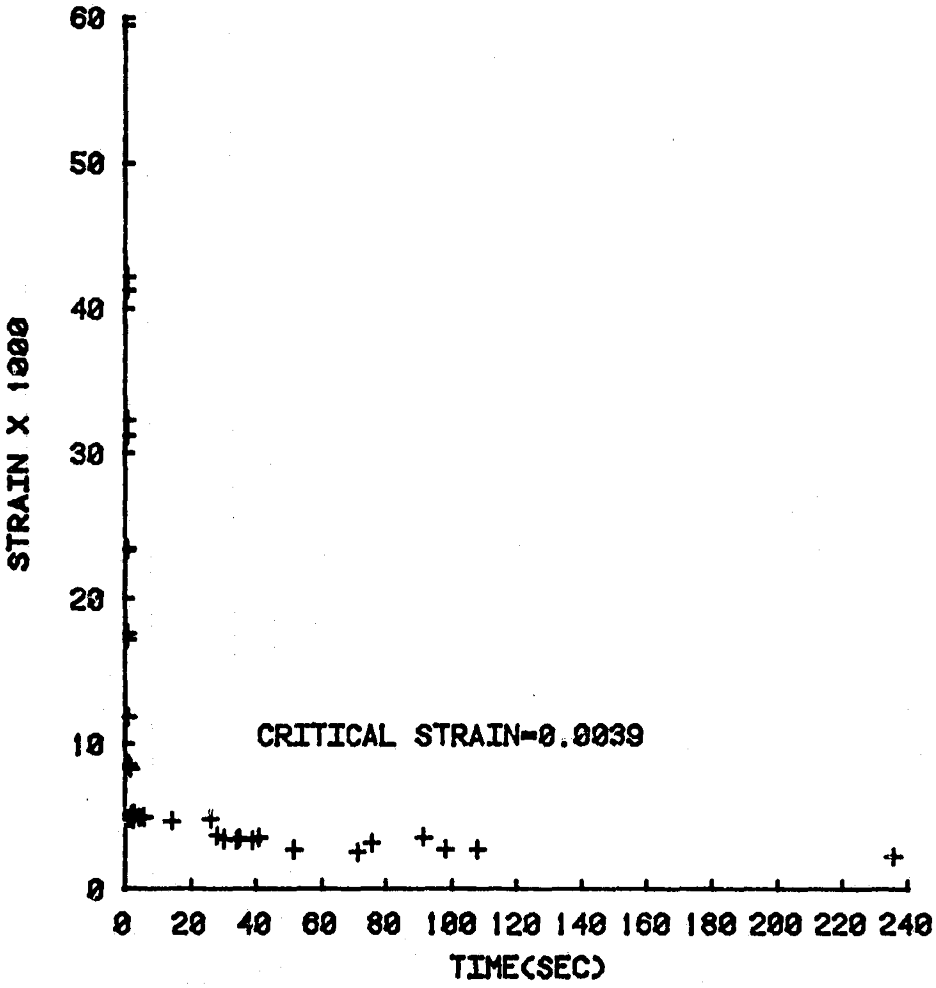


FIGURE 6. ABS/GLACIAL ACETIC ACID

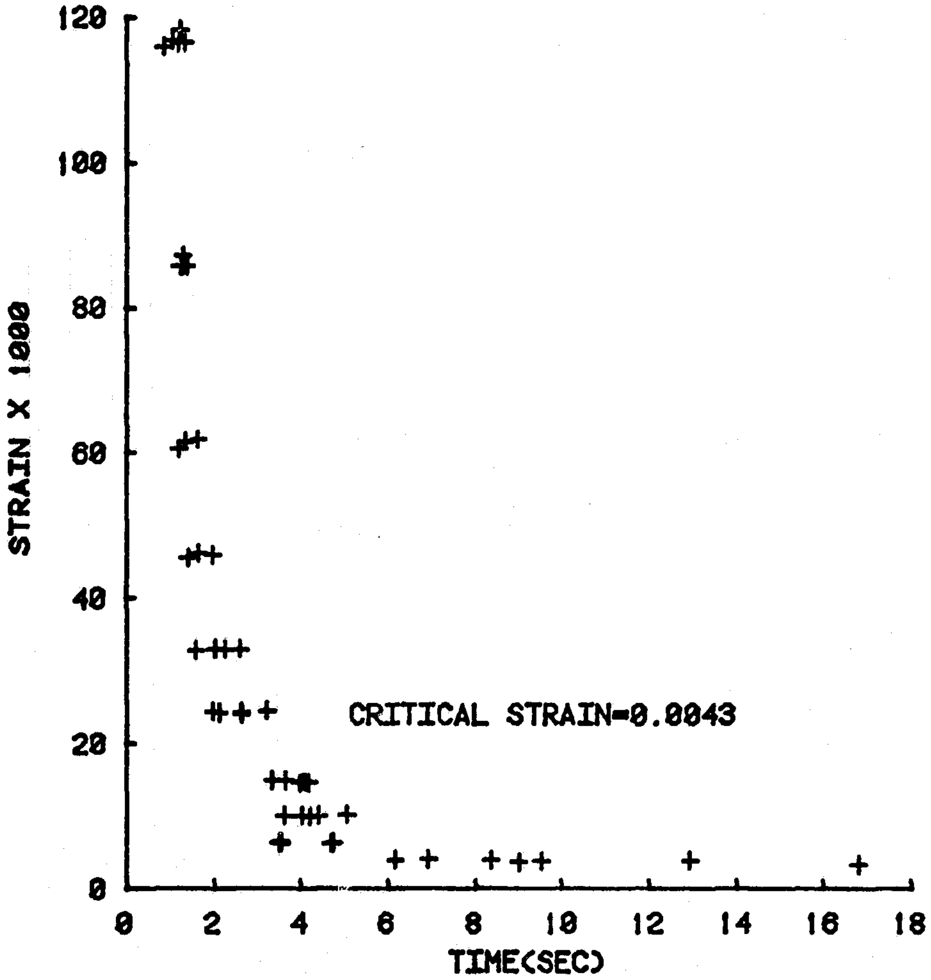


FIGURE 7. HIS/FORMIC ACID

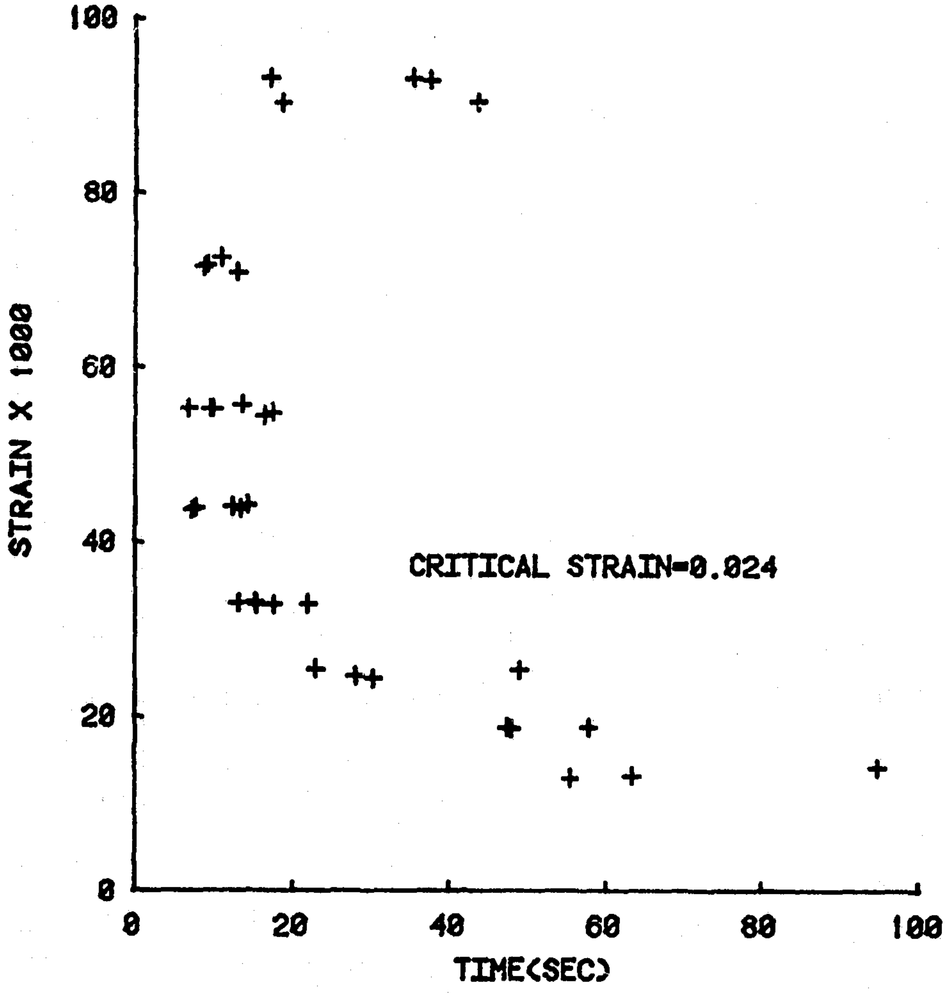


FIGURE 8. PPO/MIBK

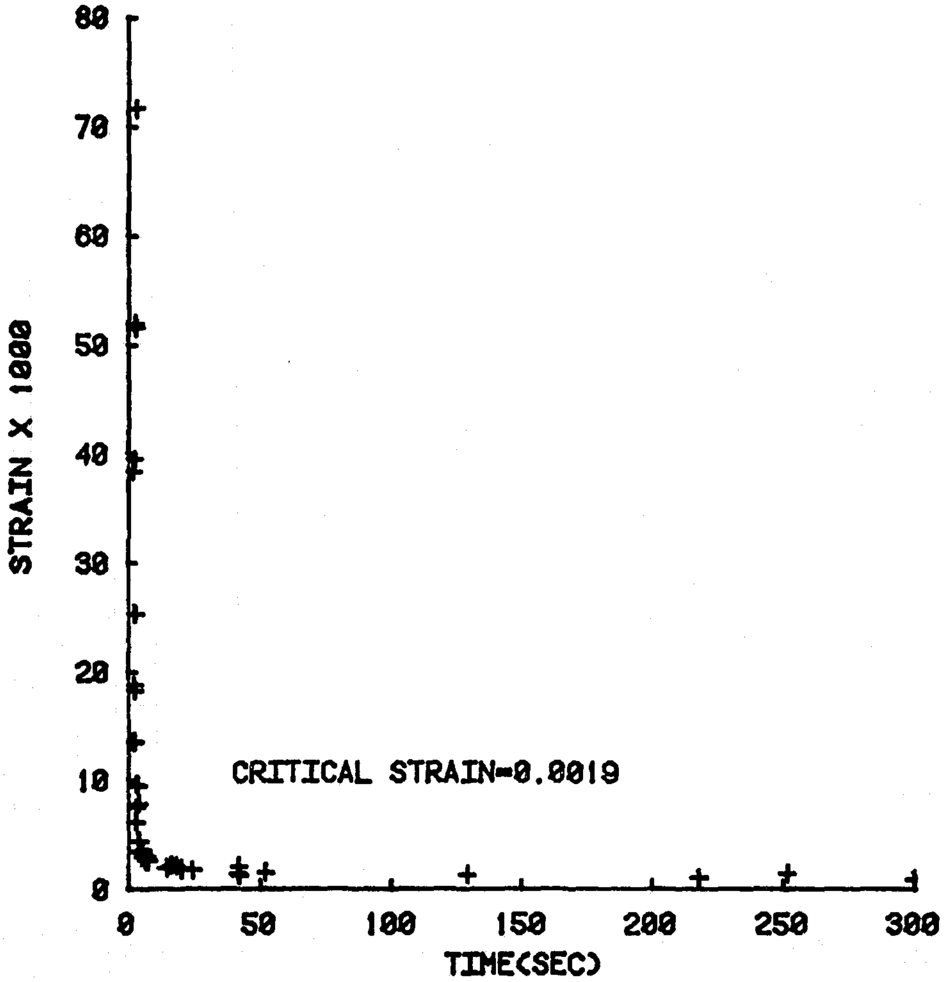


FIGURE 9. POLYCARBONATE/MIBK

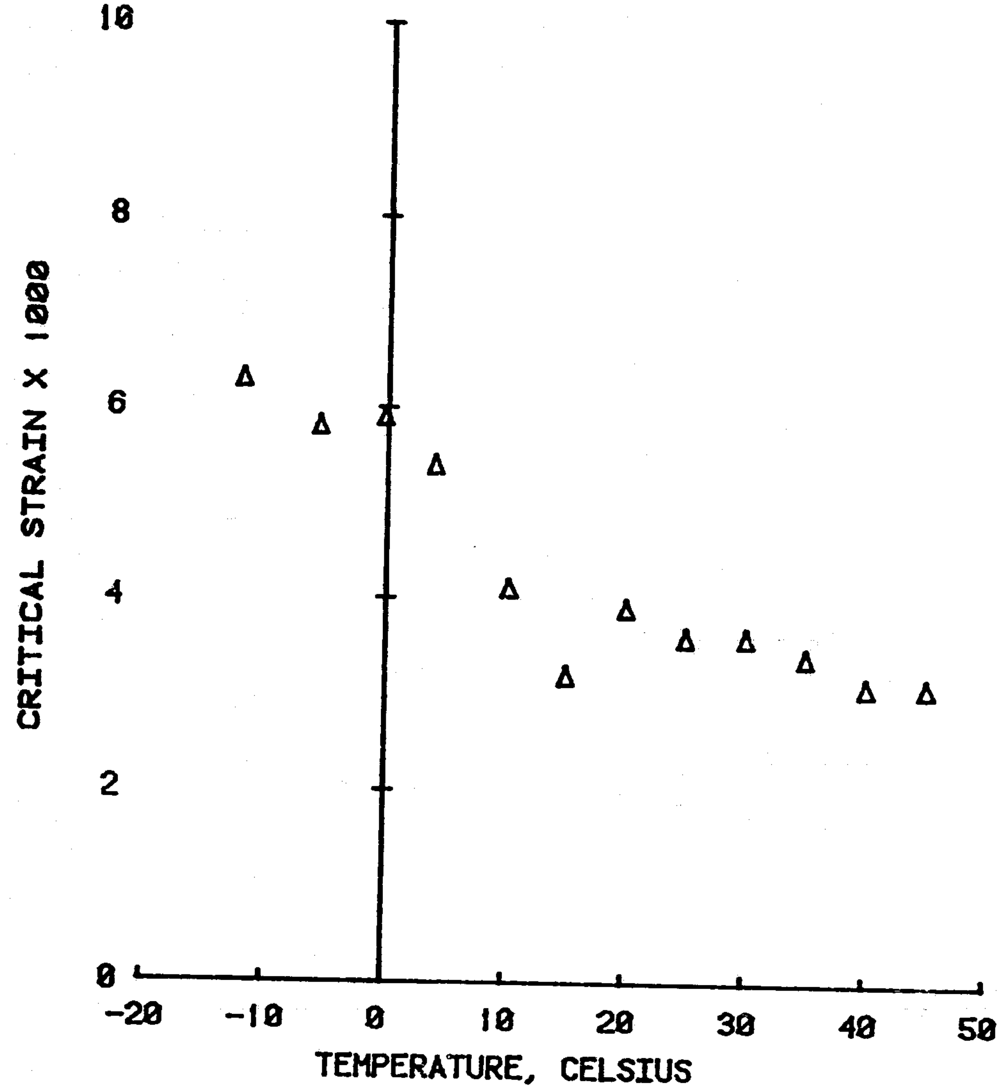


FIGURE 10. POLYCARBONATE/CYCLOHEXANONE

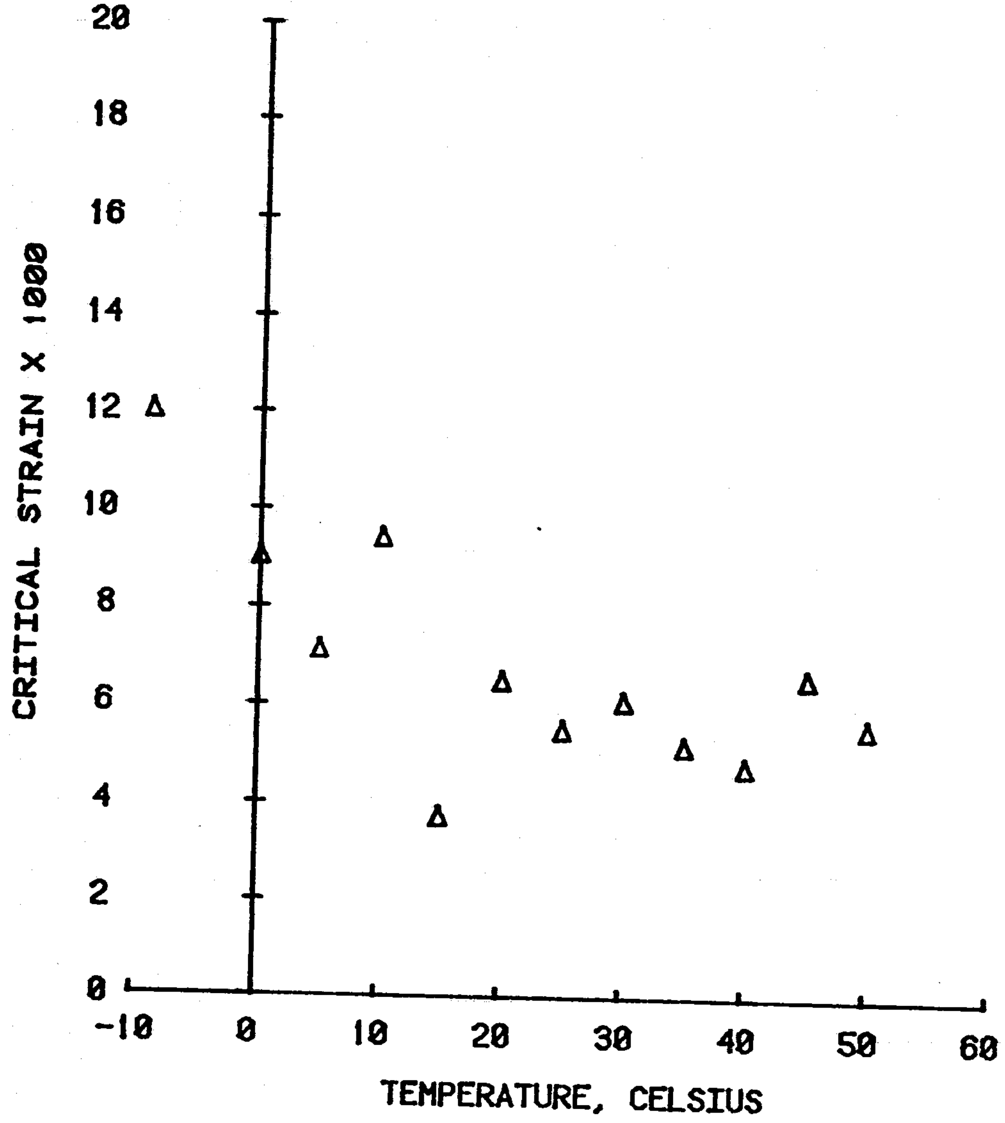


FIGURE 11. PP0/MIBK

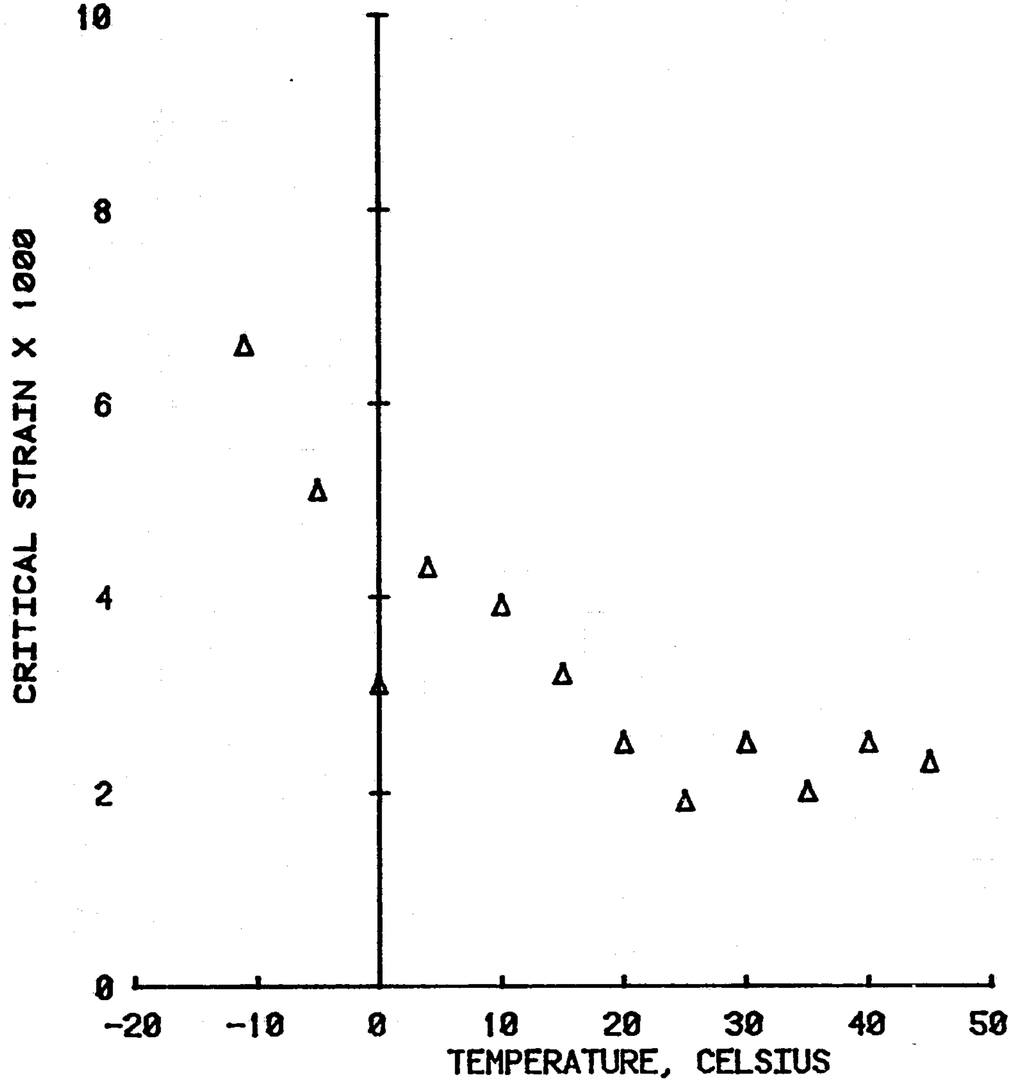


FIGURE 12. POLYCARBONATE/CYCLOHEXANONE, 0 C

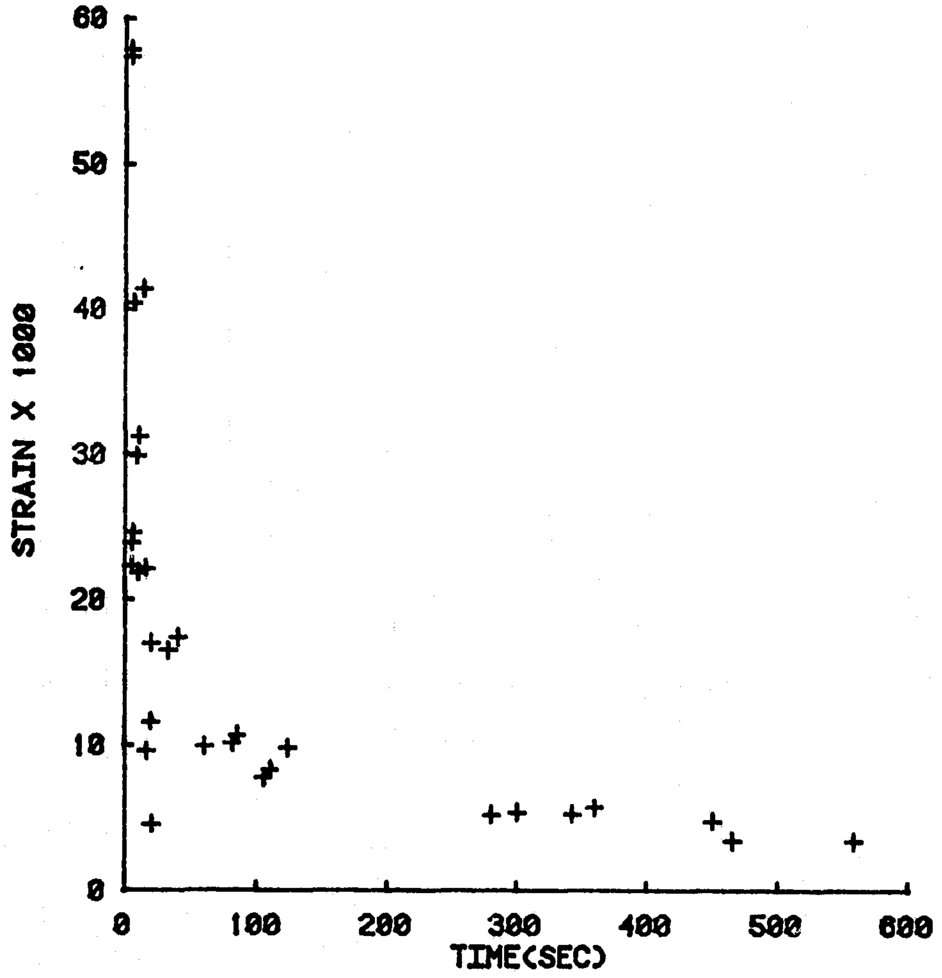


FIGURE 13. POLYCARBONATE/CYCLOHEXANONE, 25 C

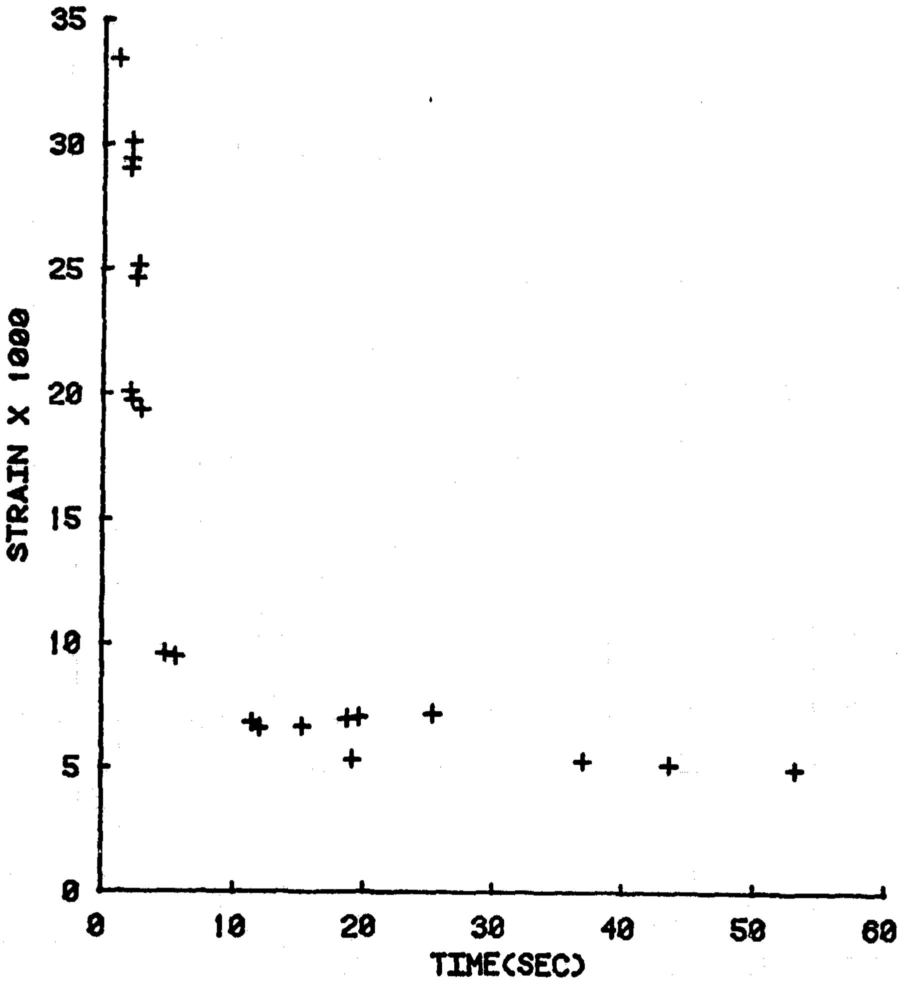


FIGURE 14. POLYCARBONATE/CYCLOHEXANONE, 50 C

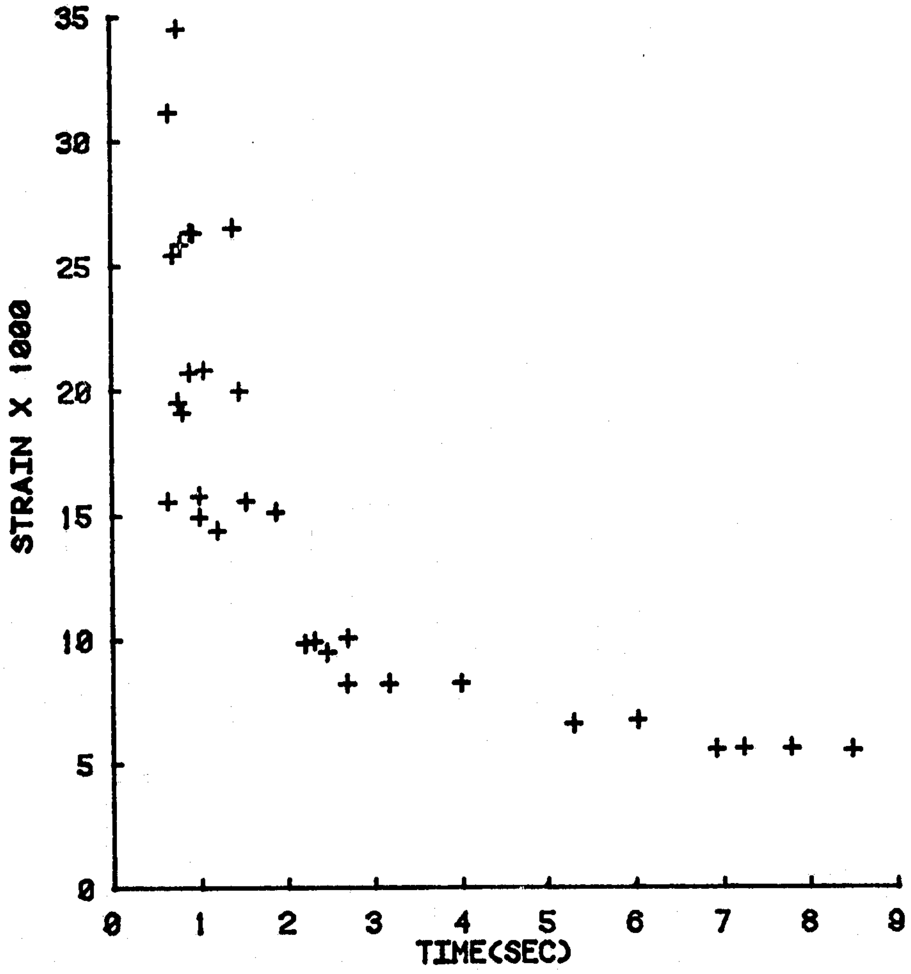
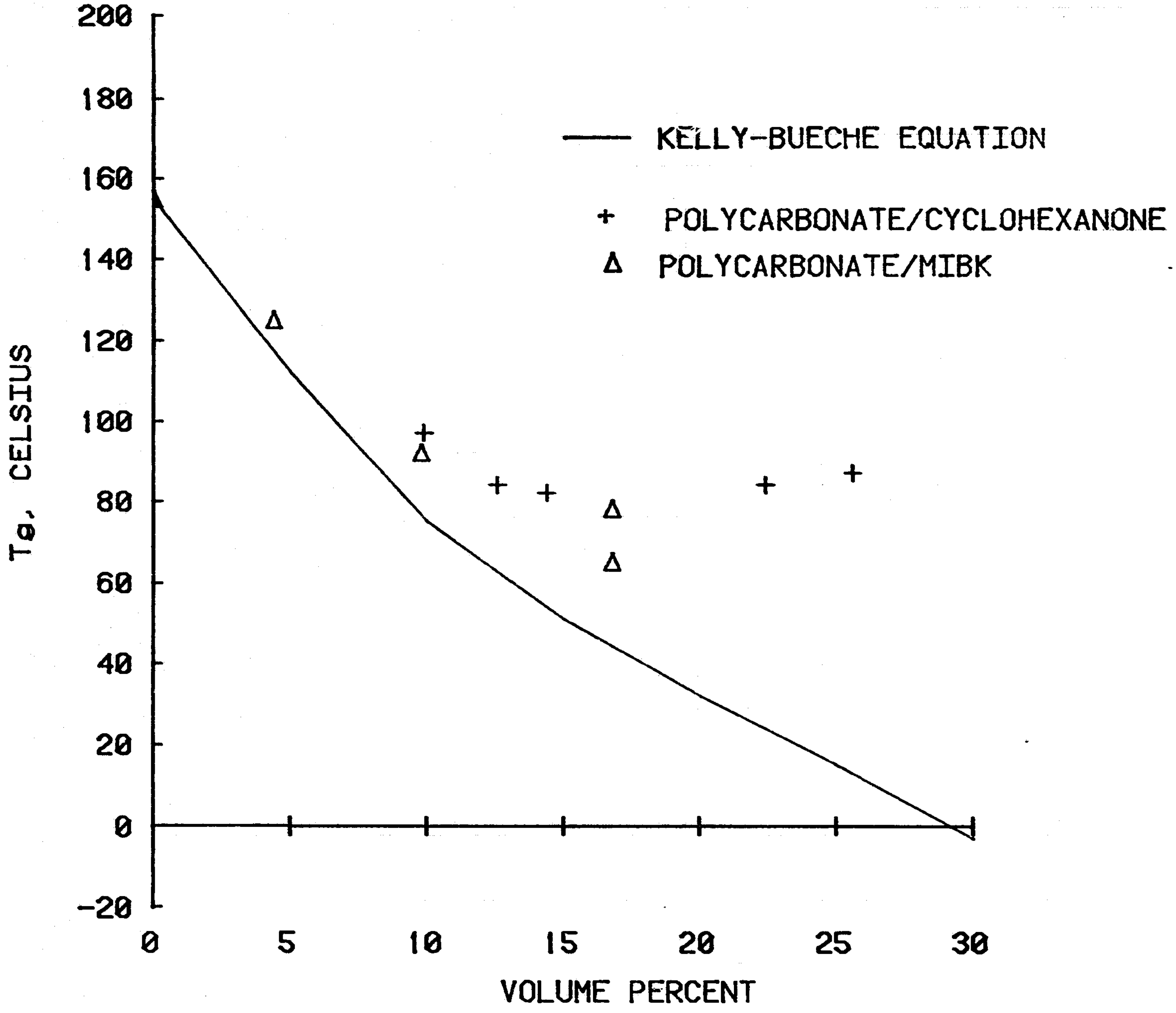


FIGURE 15. GLASS TRANSITION TEMPERATURE(T_g) VS SOLVENT CONC.



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7. ACKNOWLEDGMENTS.

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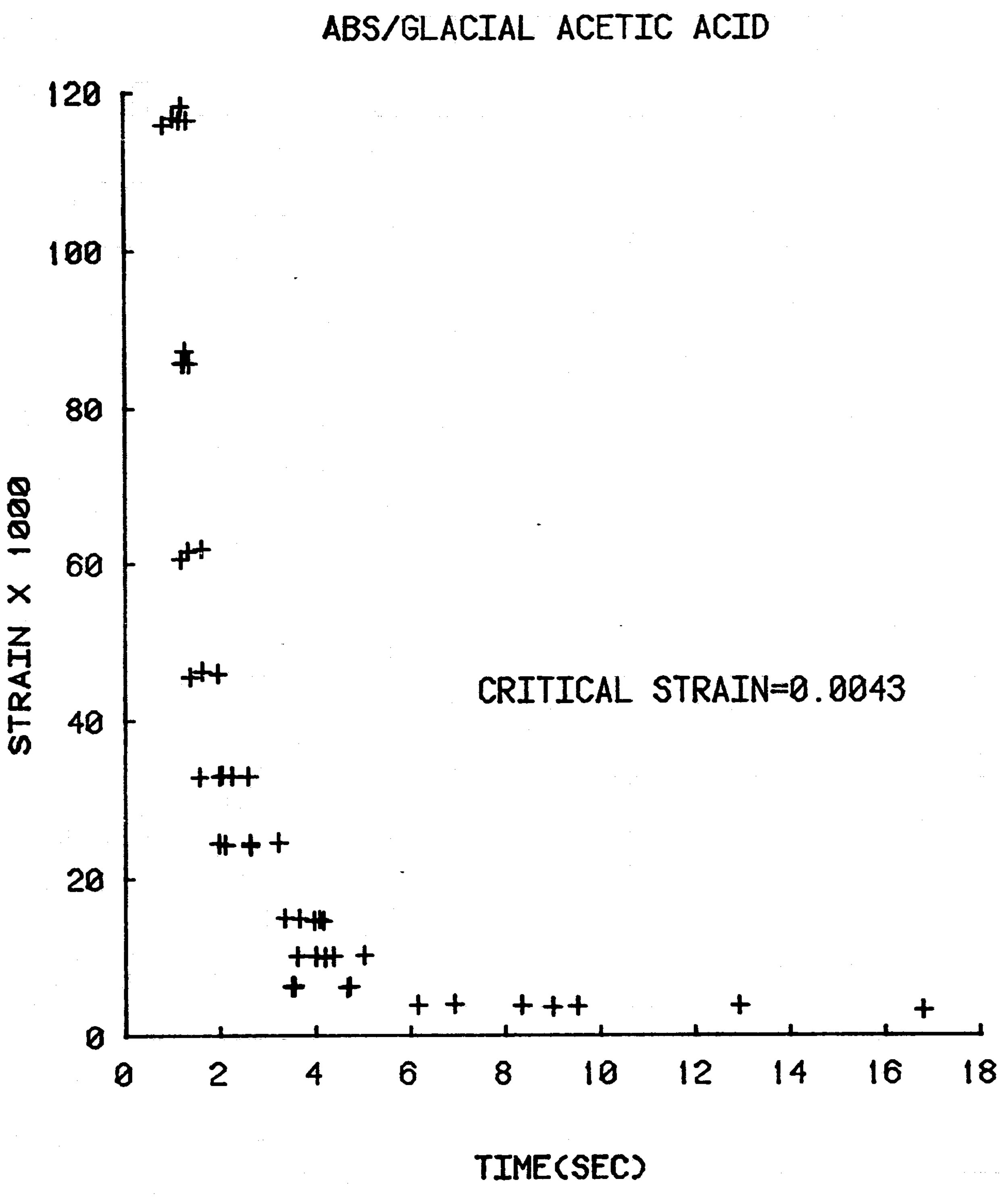
APPENDIX

ABS/GLACIAL ACETIC ACID
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20
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0
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10
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16
18
TIME(SEC)
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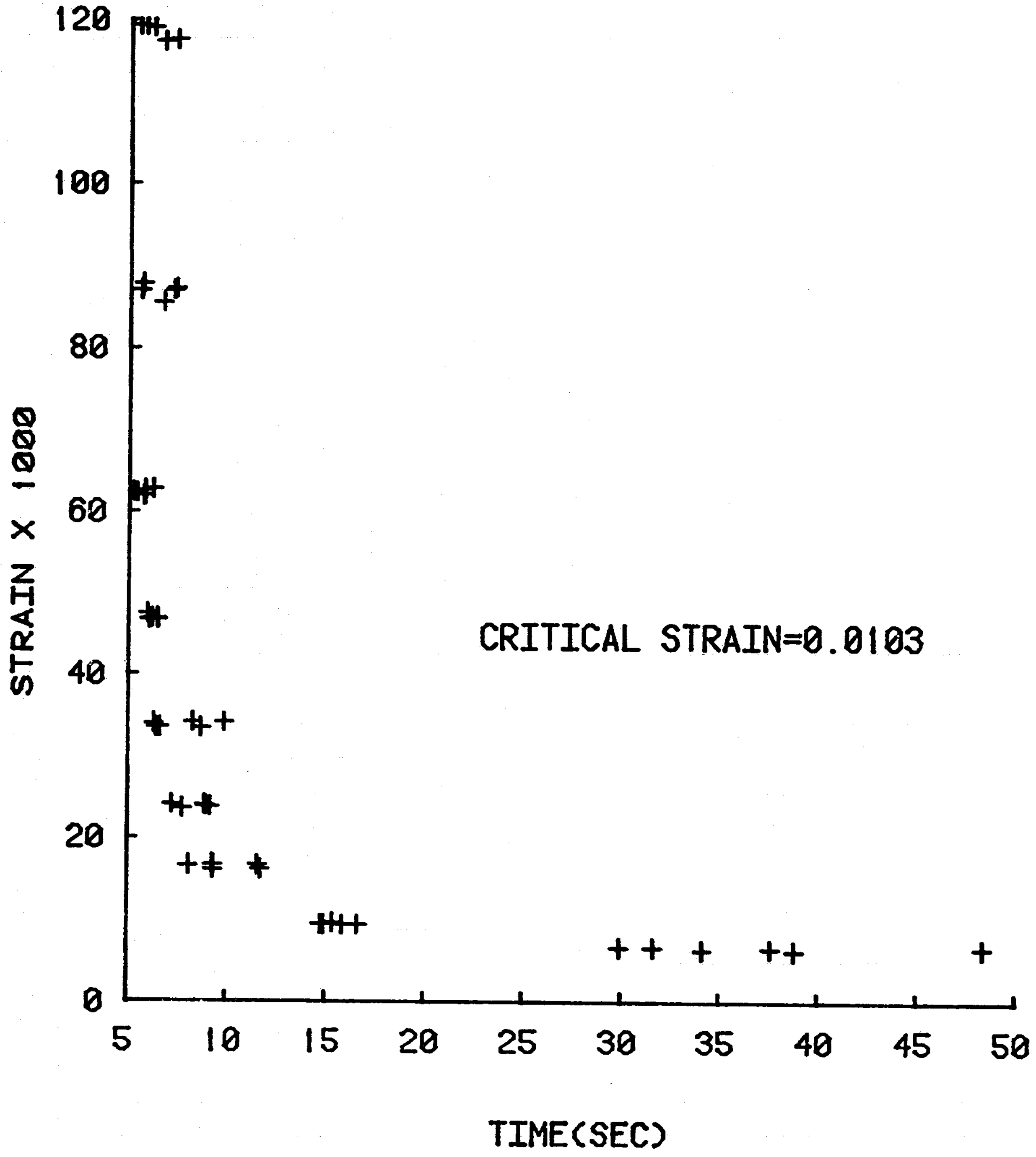
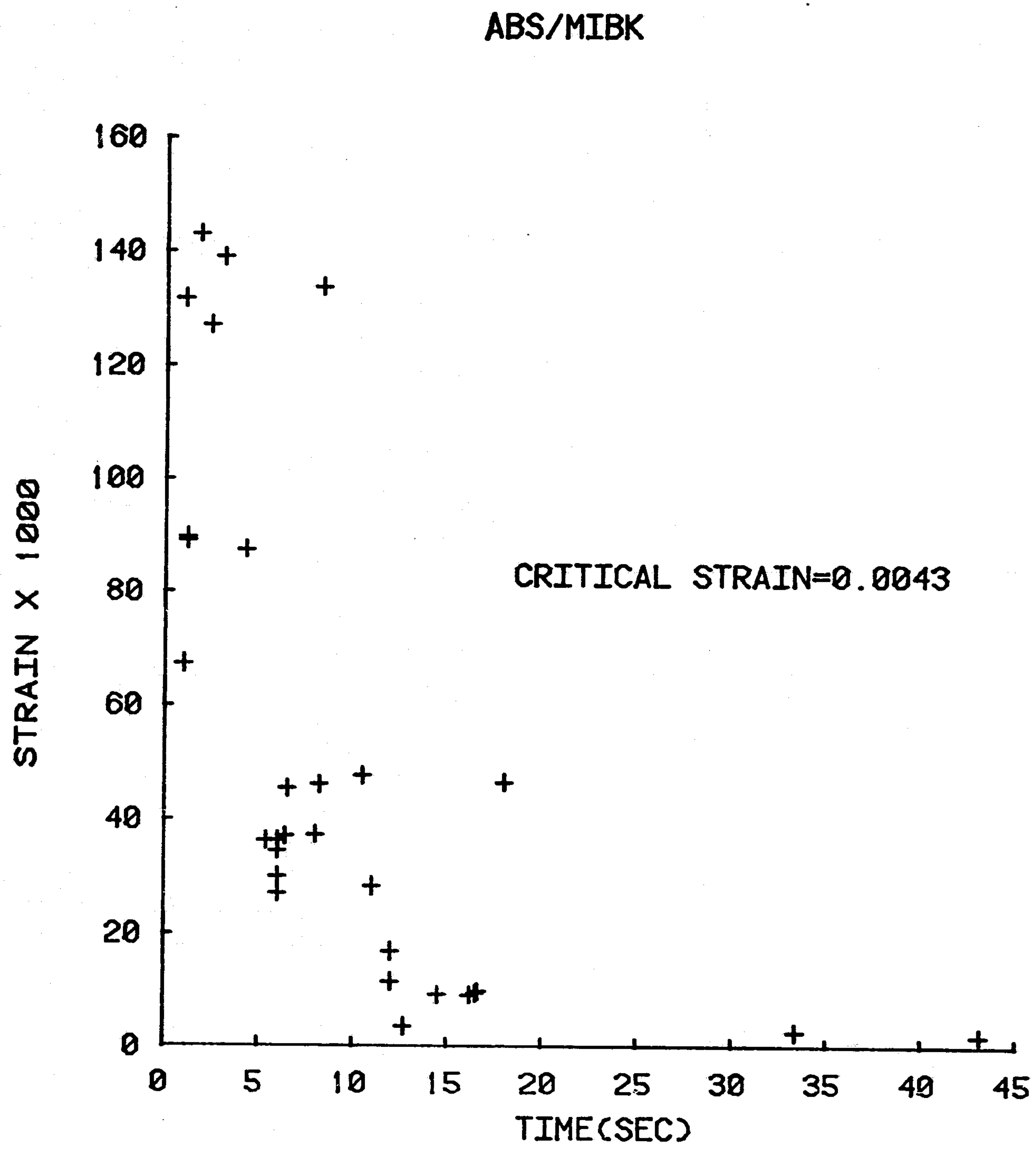
ABS/N-BUTYL BROMIDE



ABS/MIBK
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40
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TIME(SEC)
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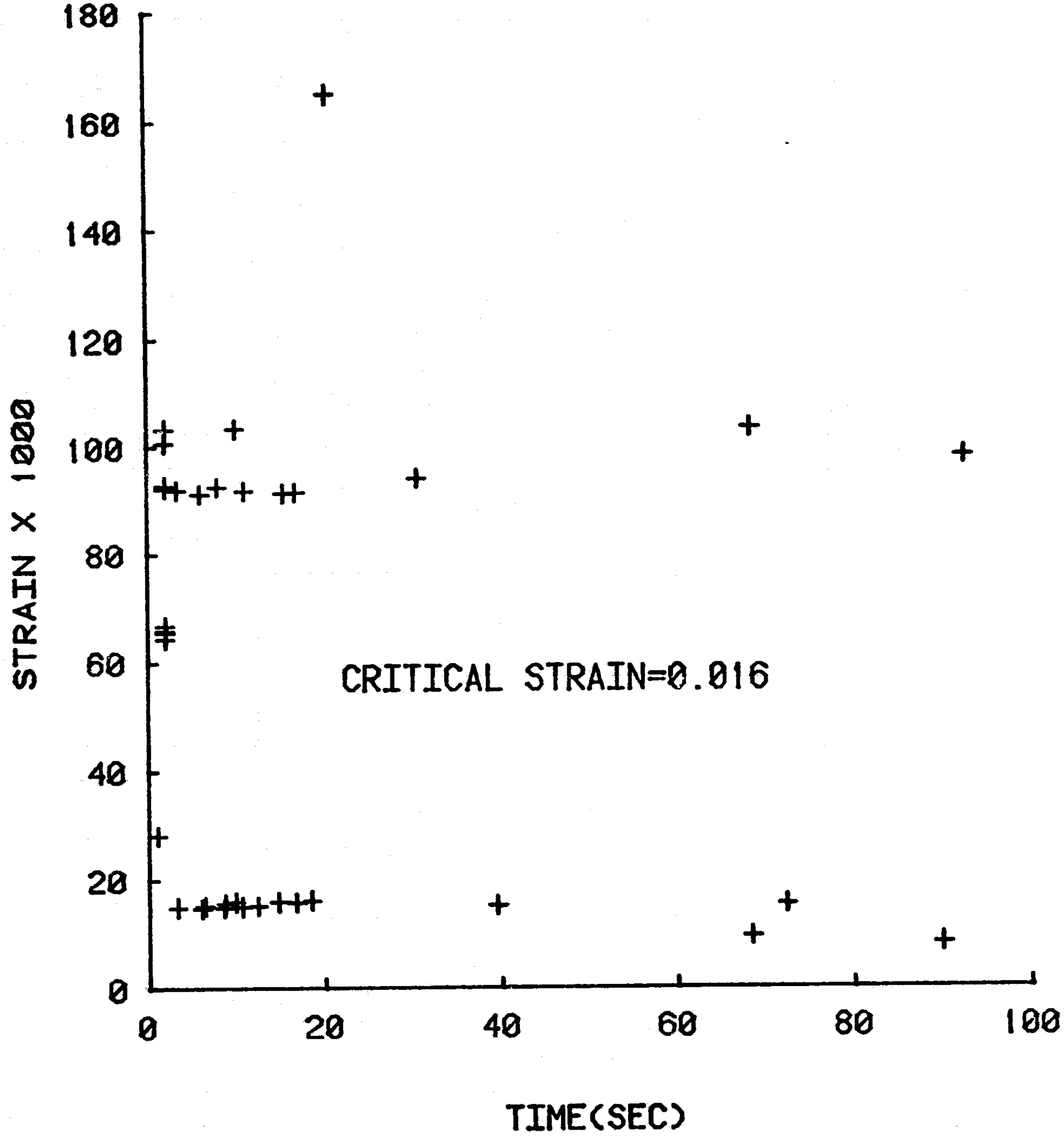

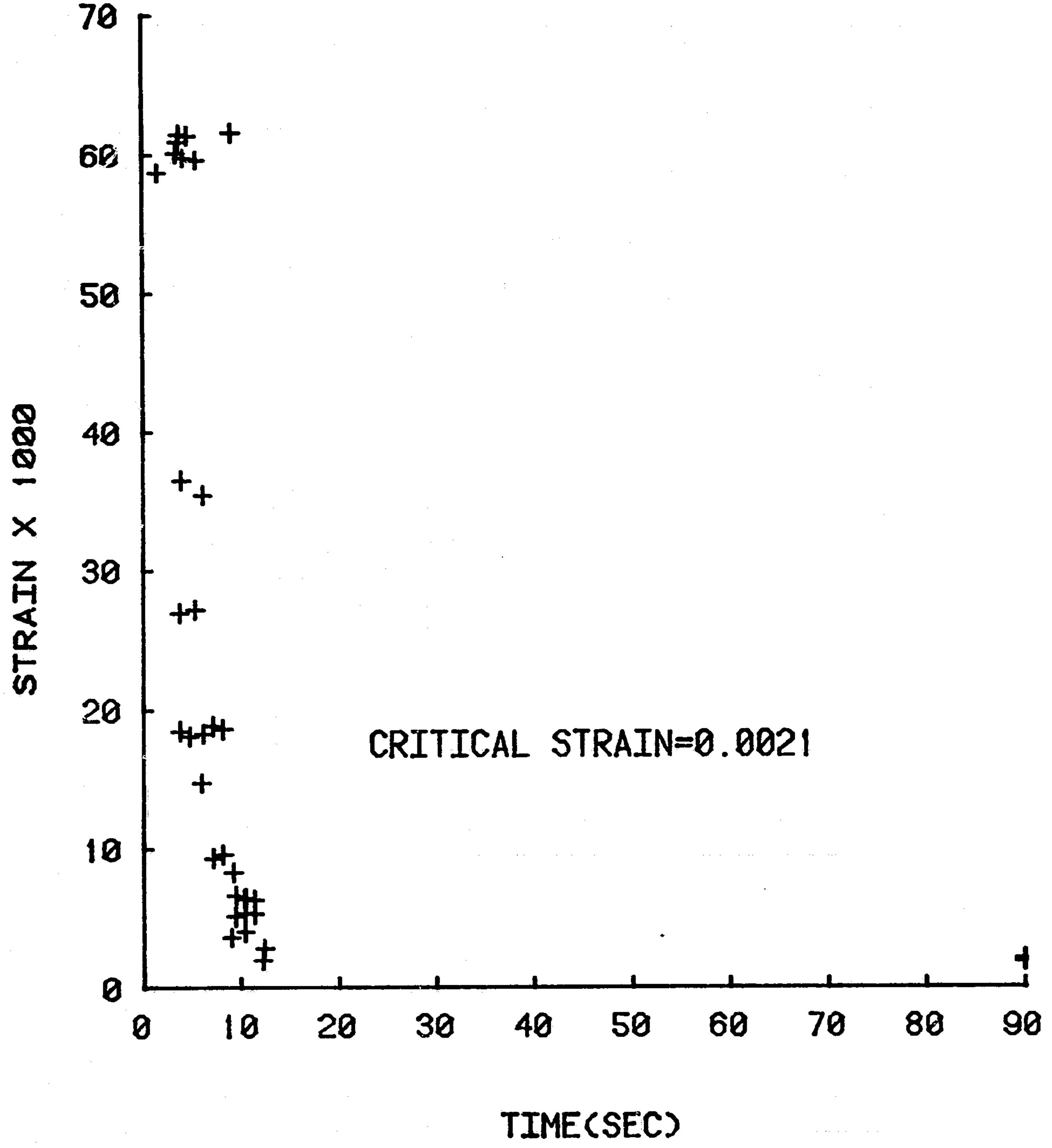

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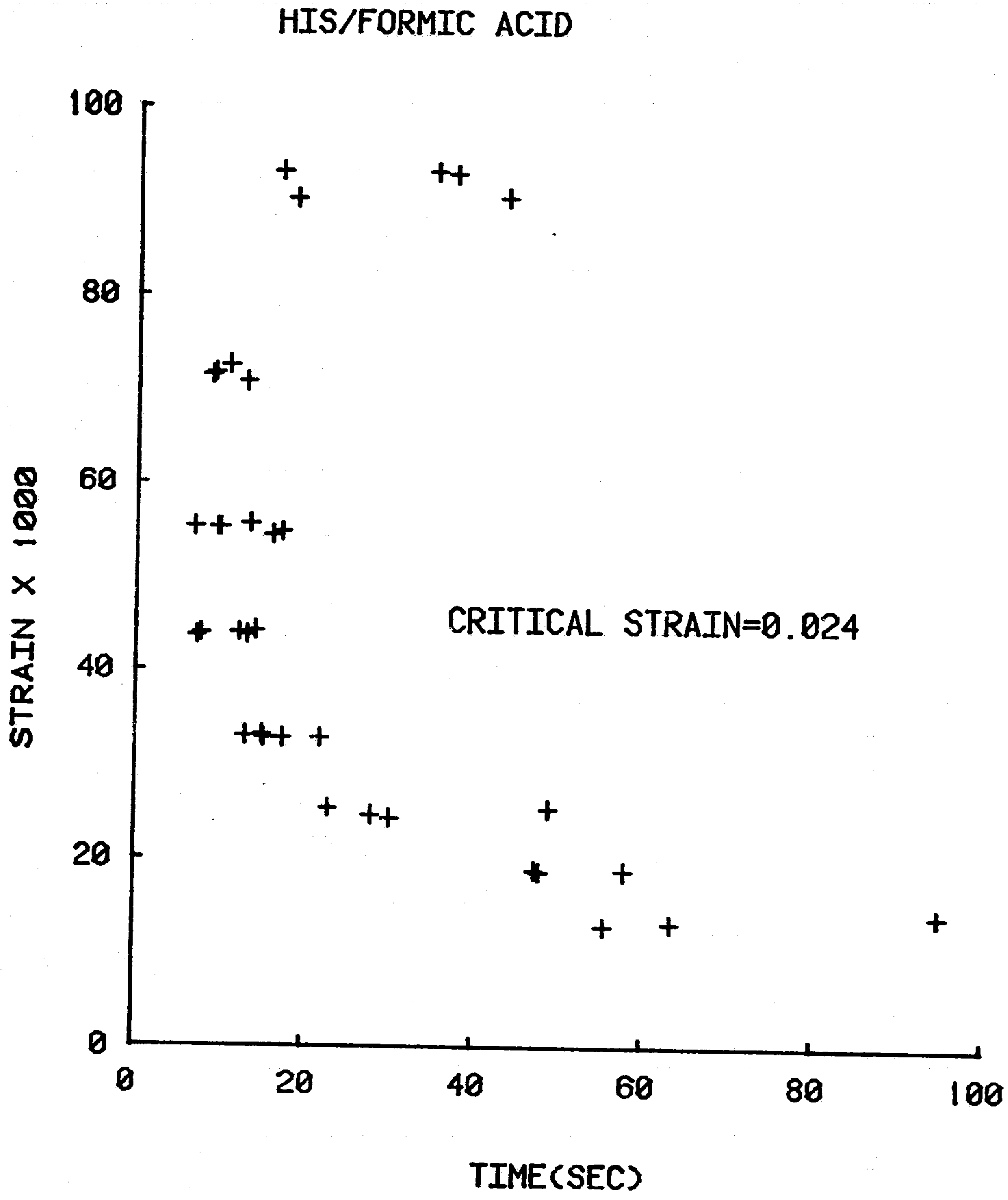
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100

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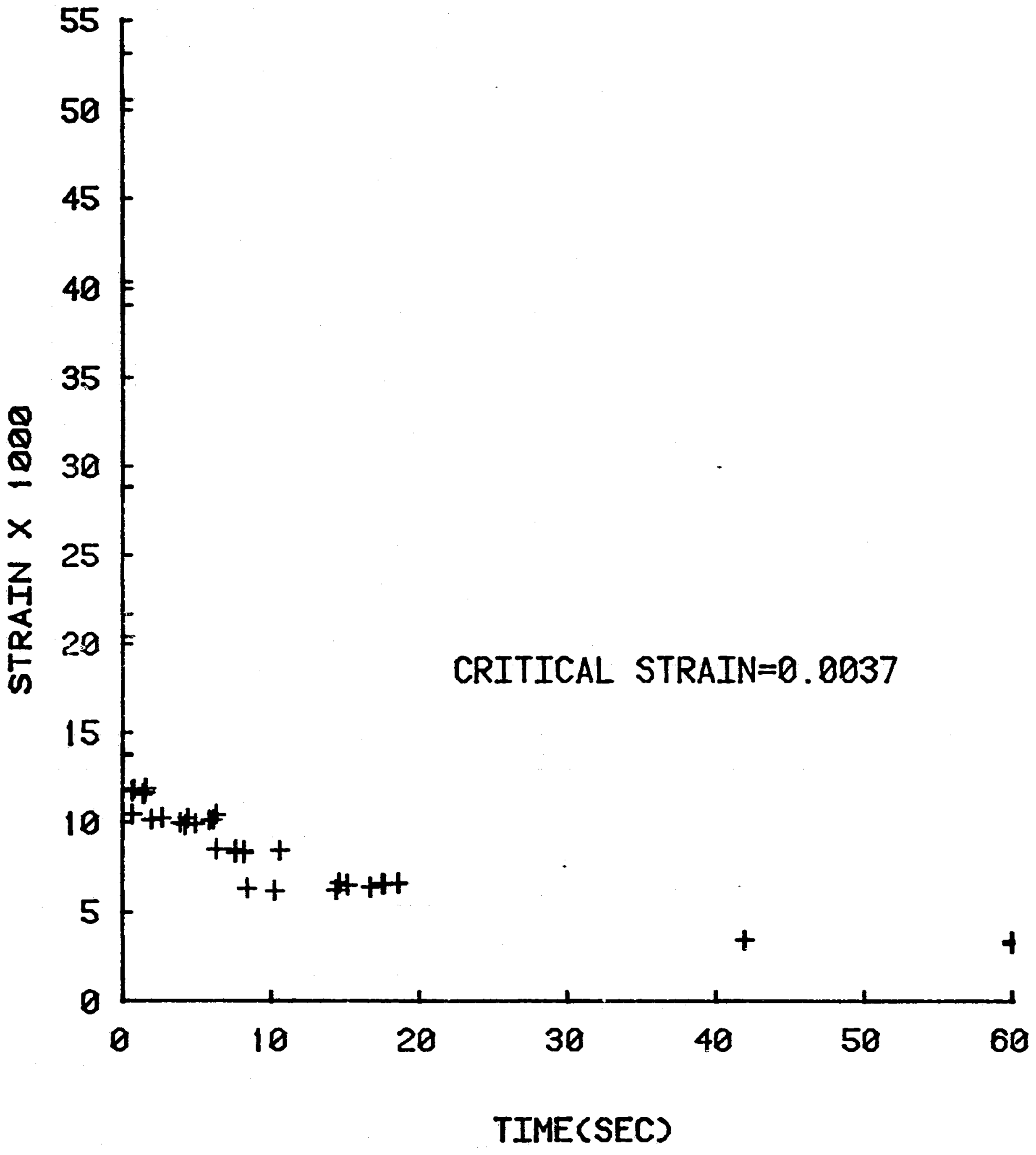

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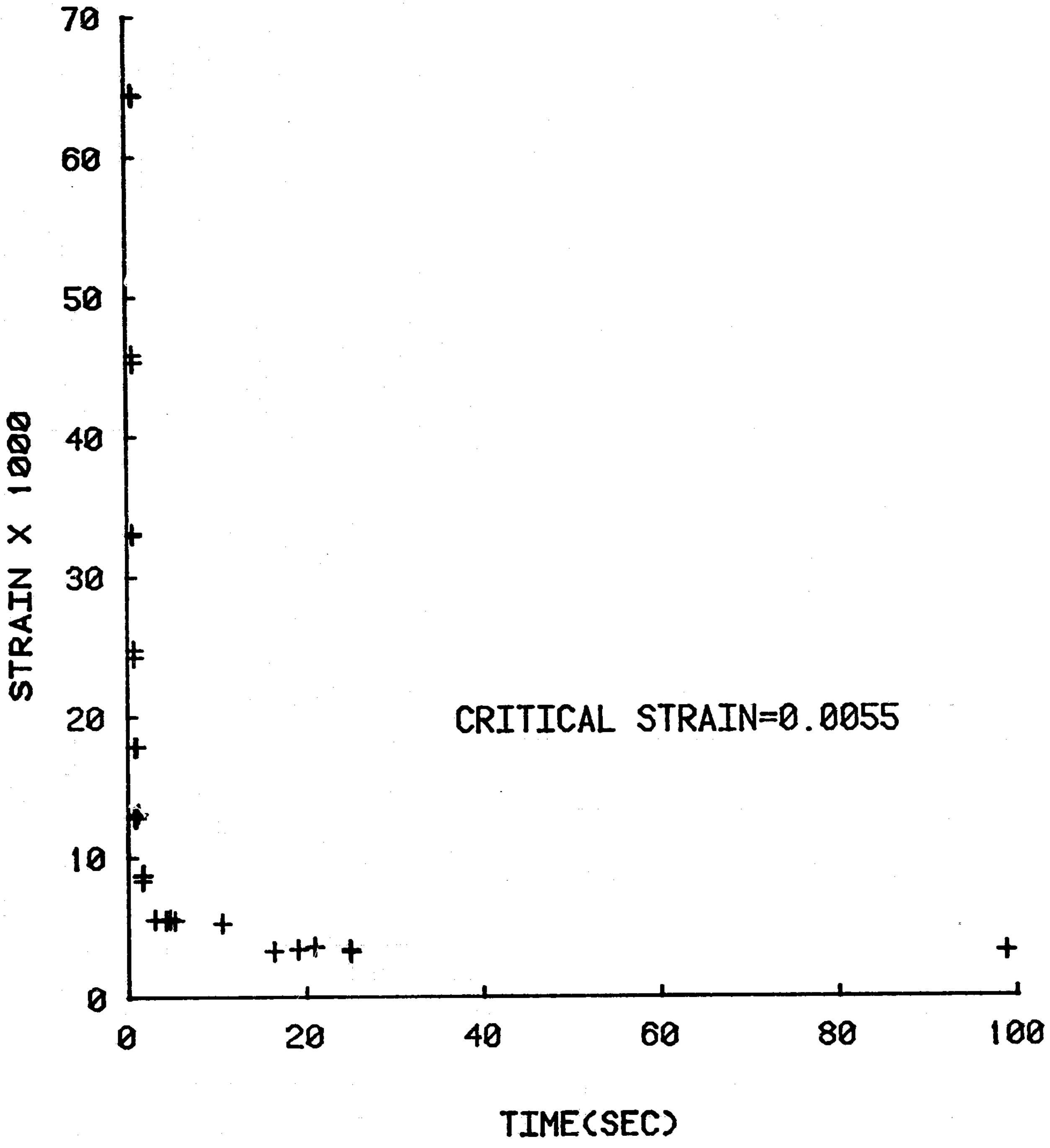

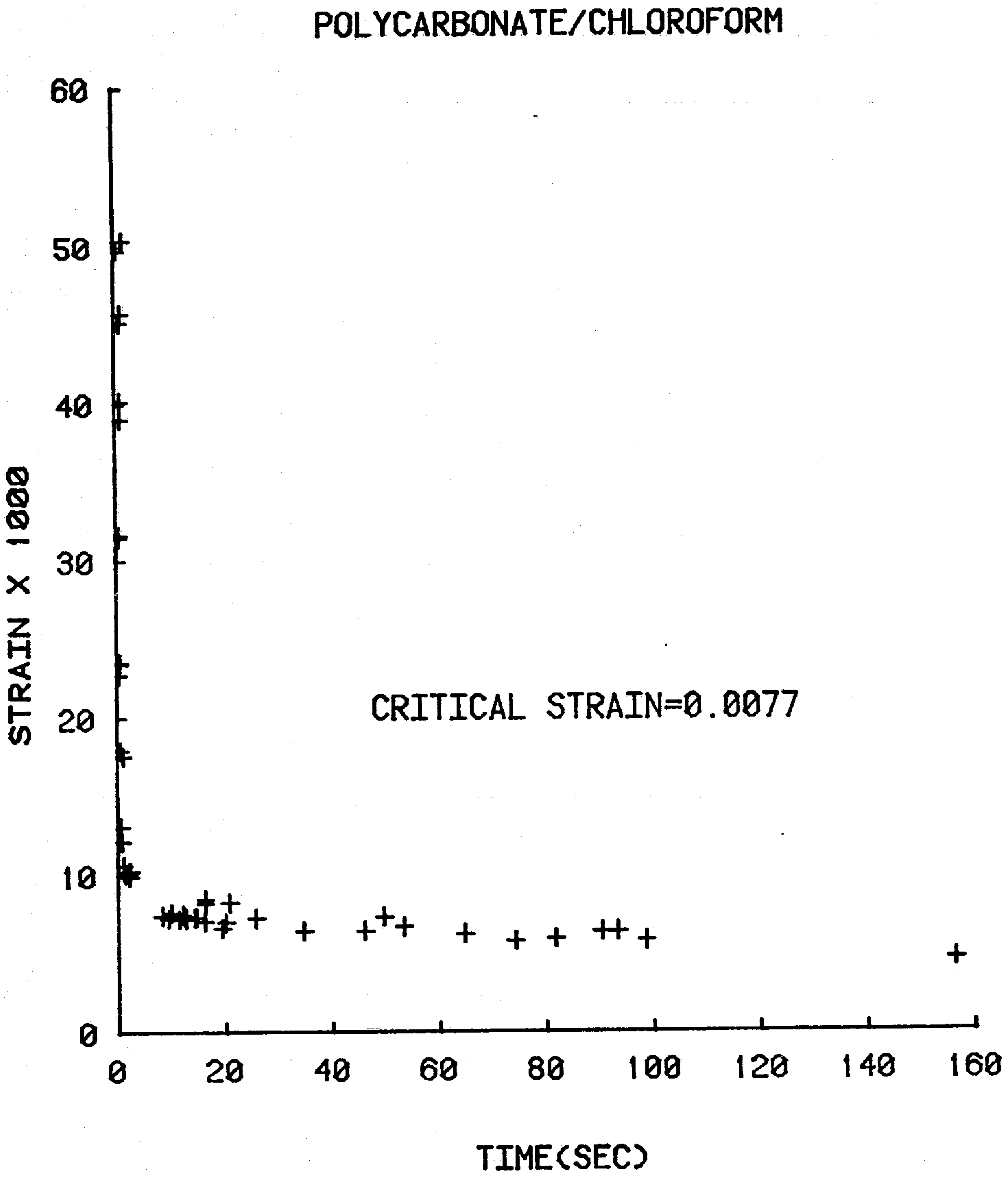
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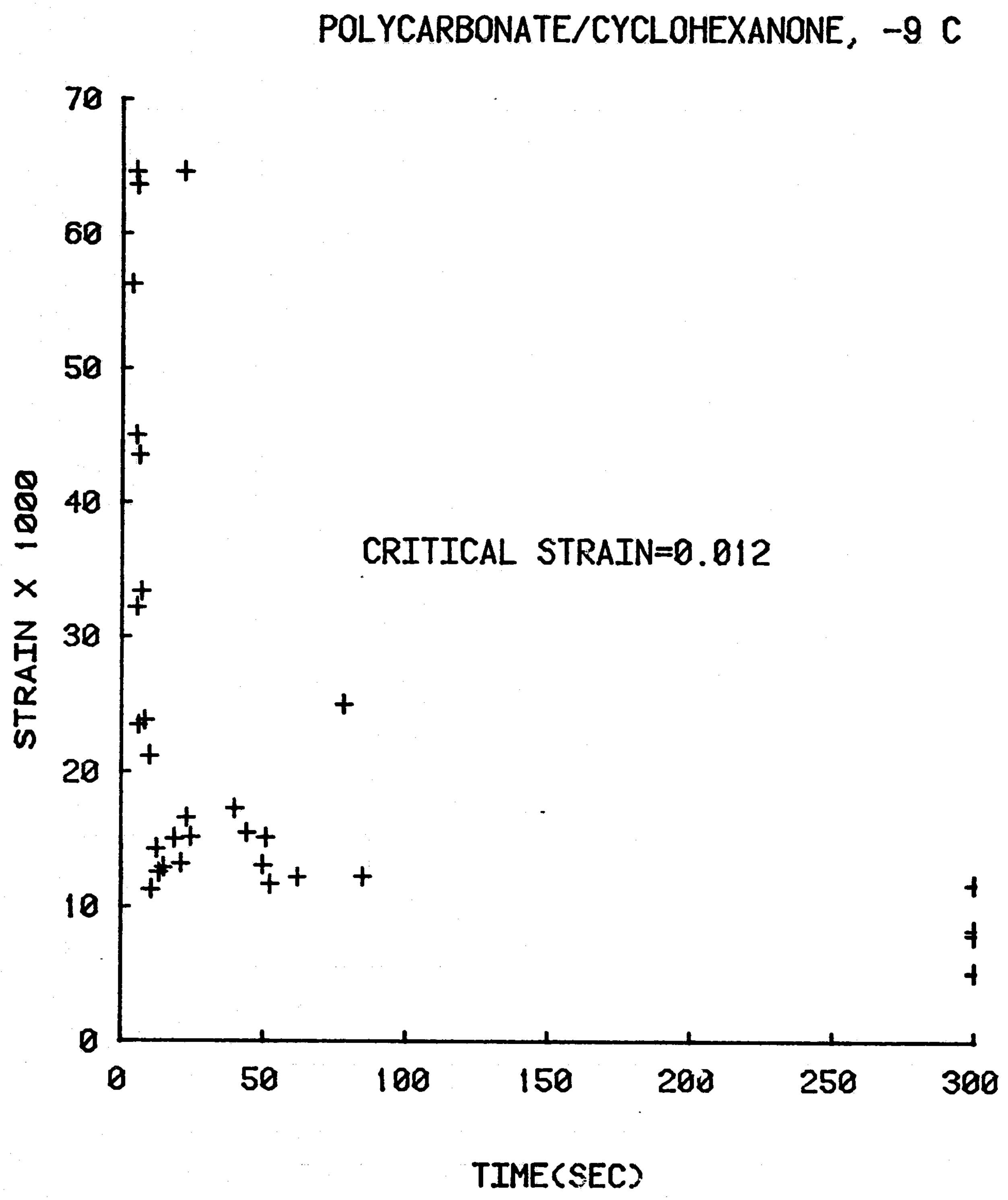
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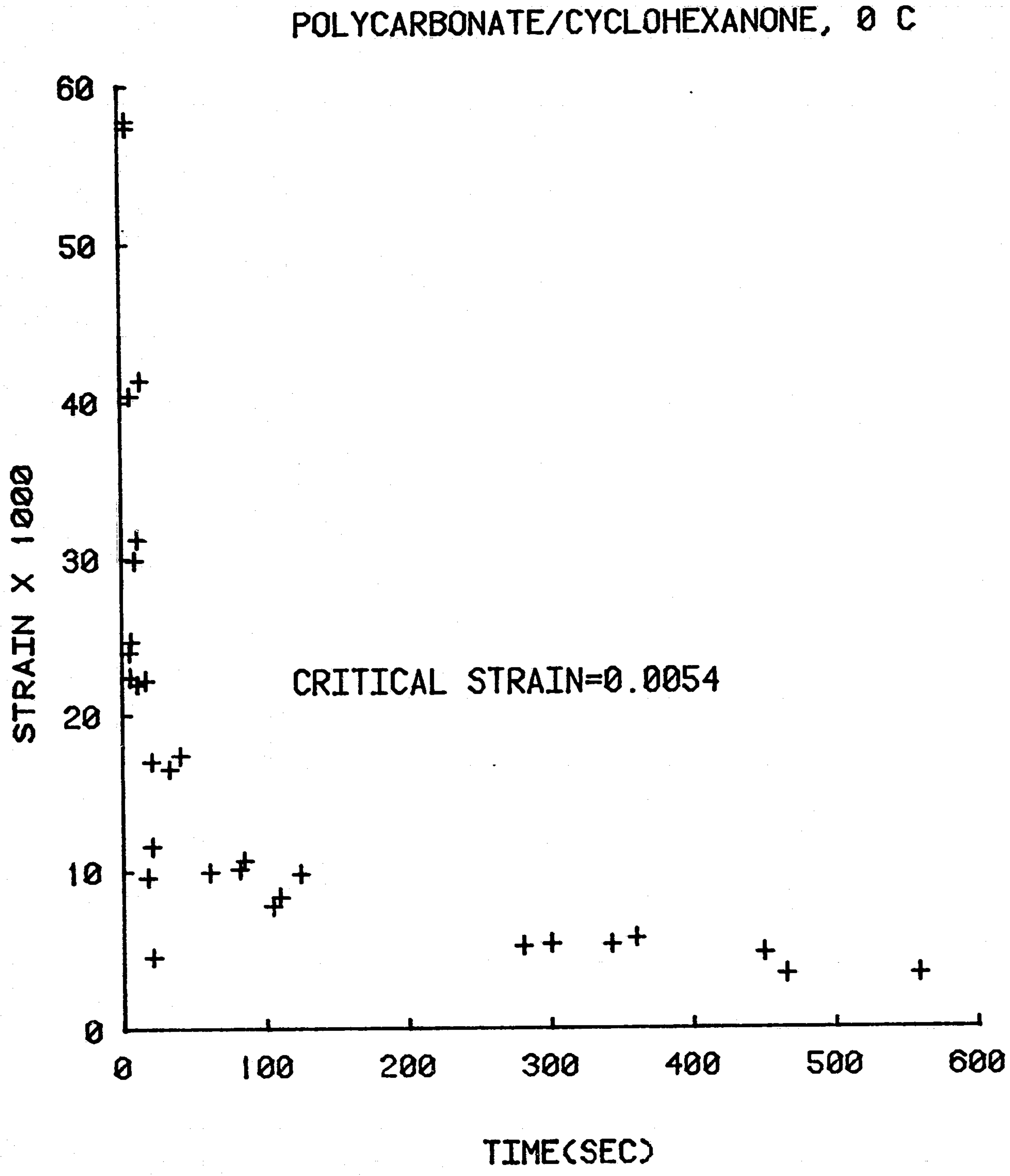
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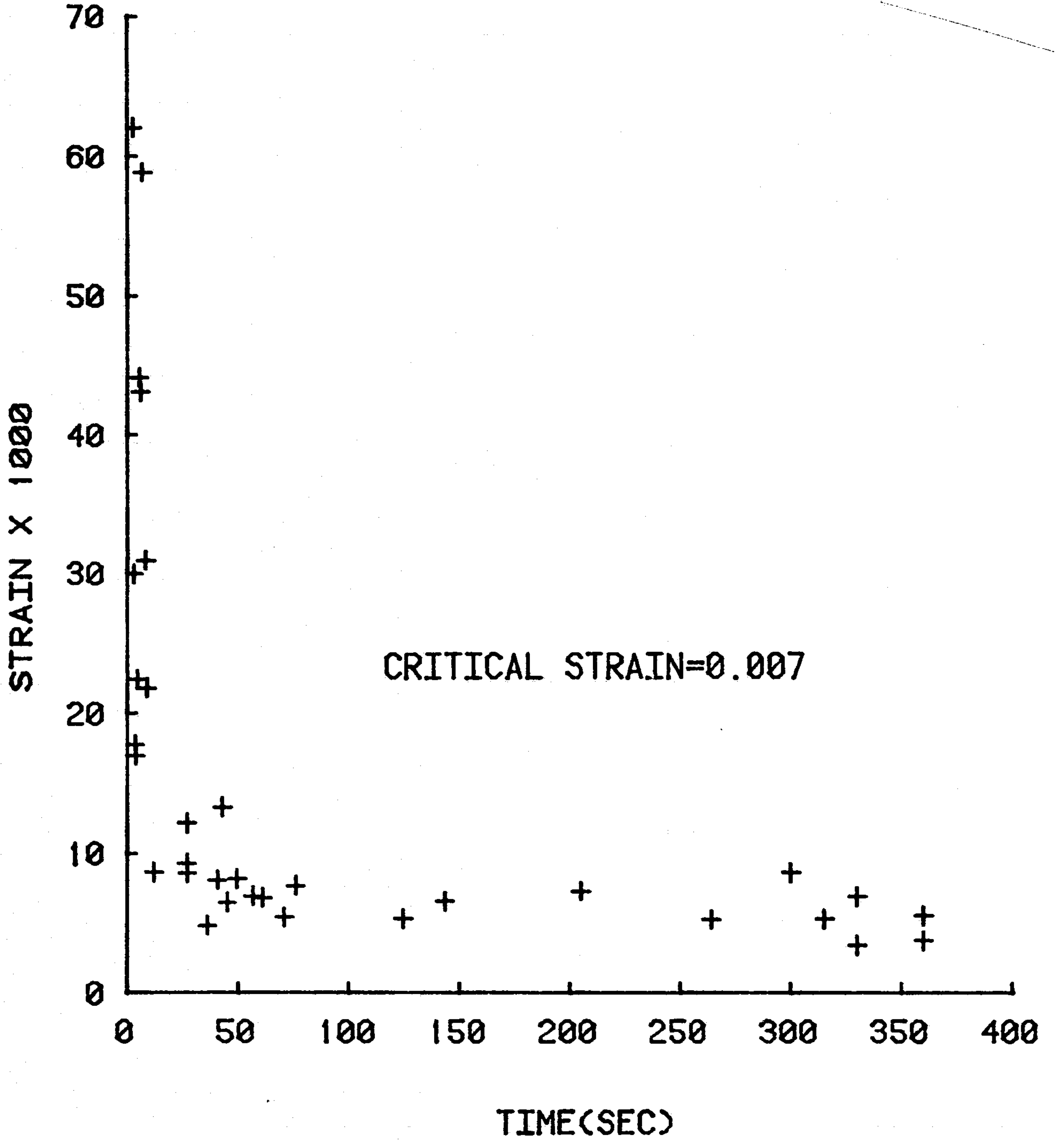

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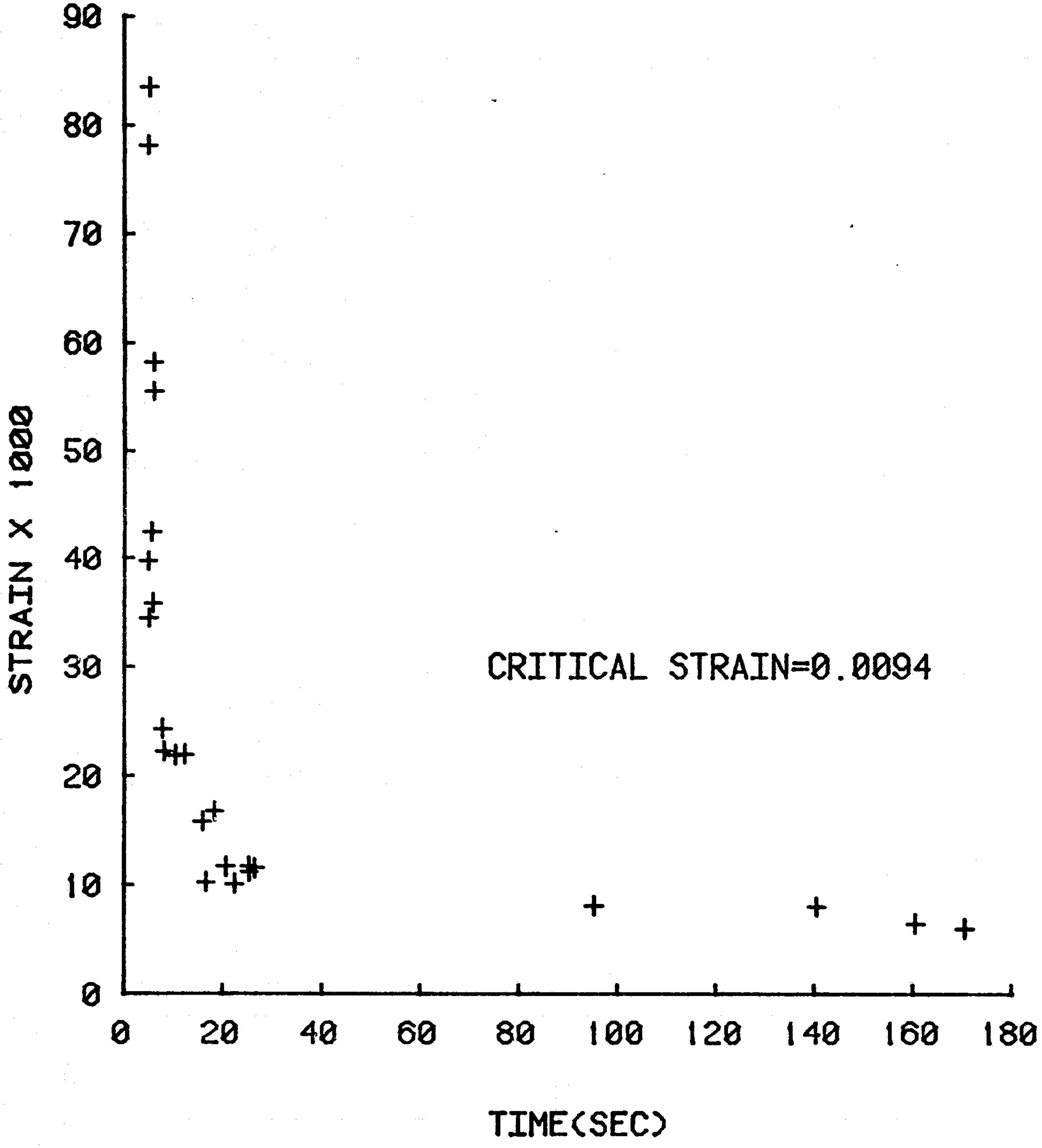
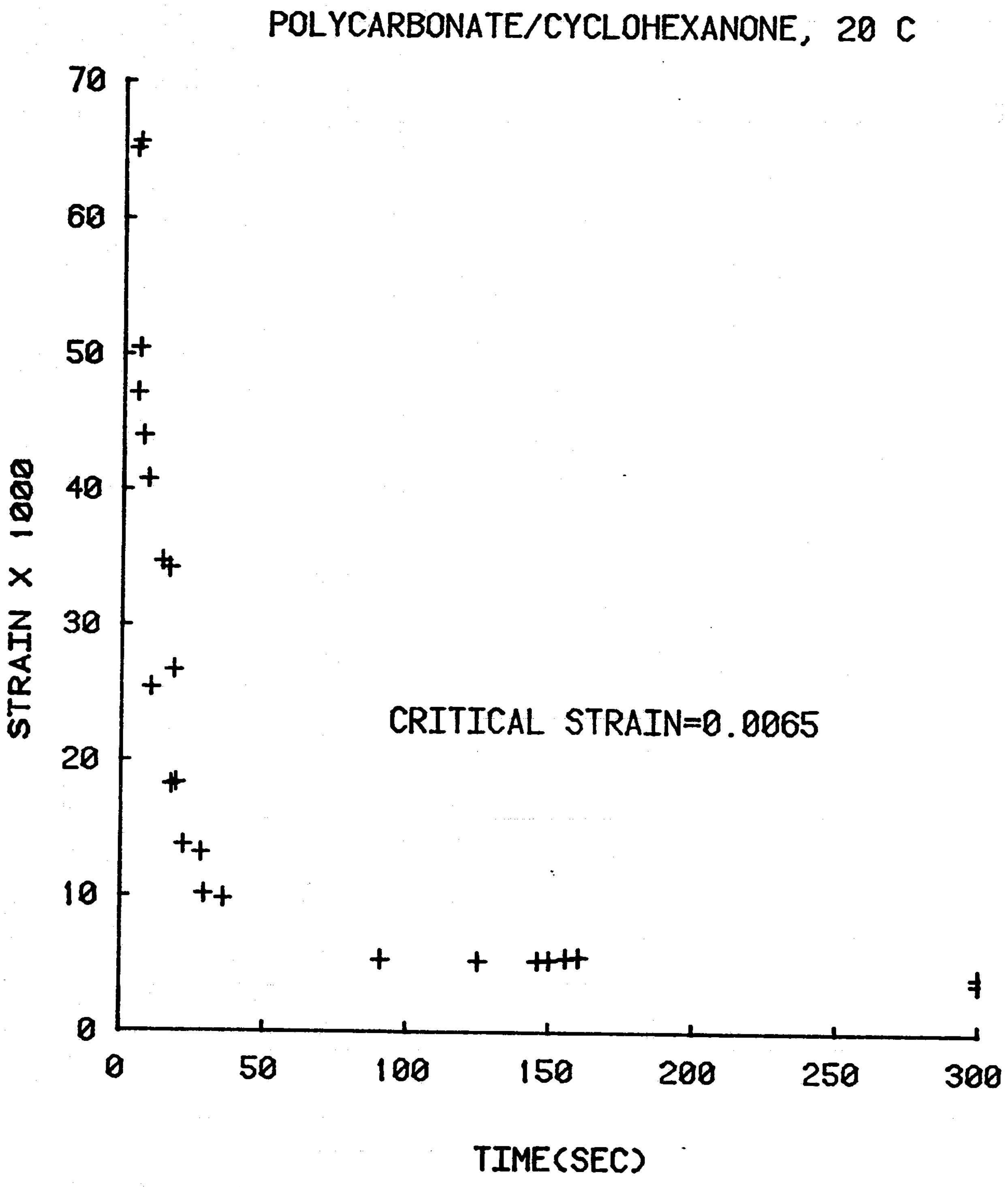
POLYCARBONATE/CYCLOHEXANONE, 10 C

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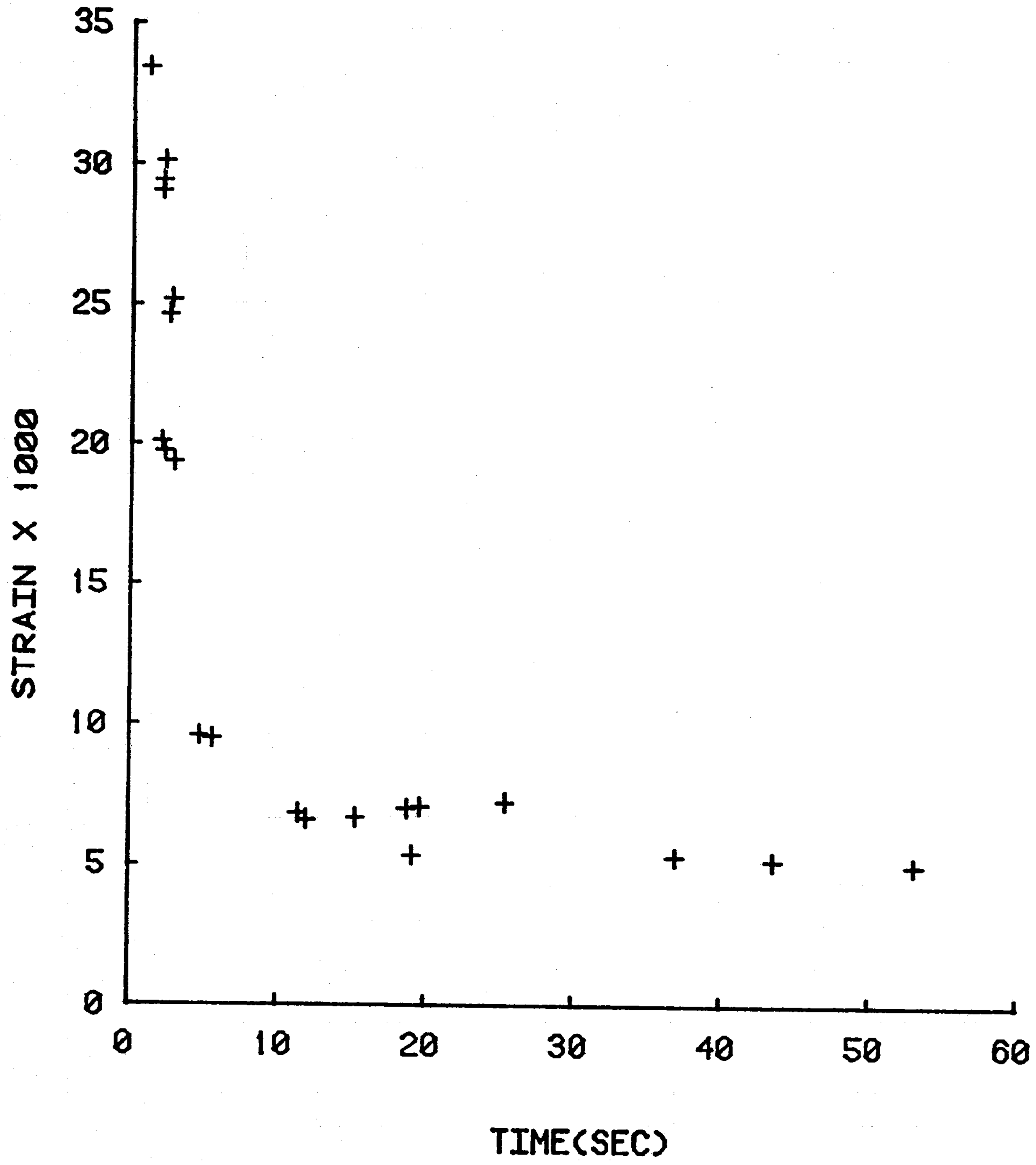

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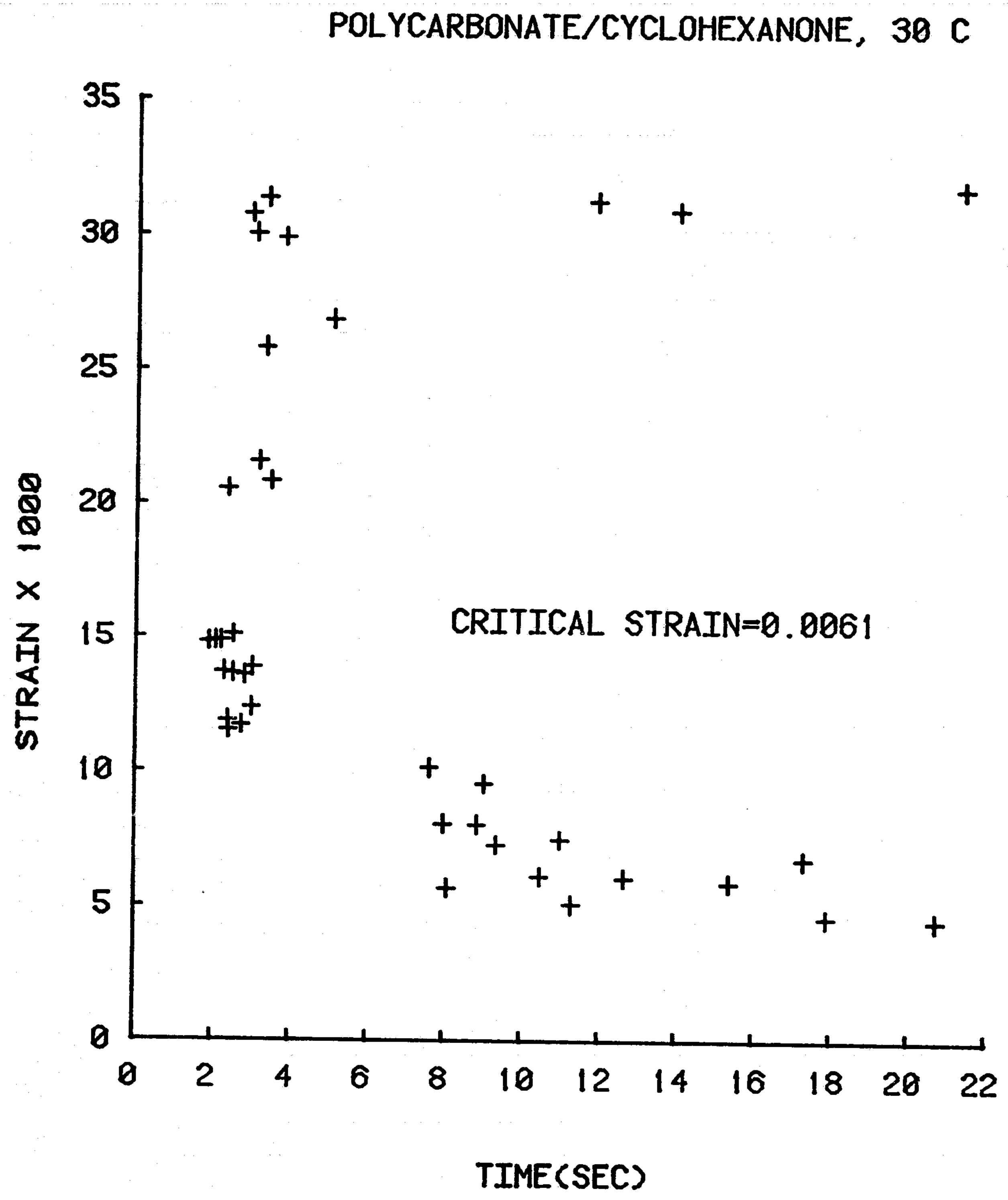
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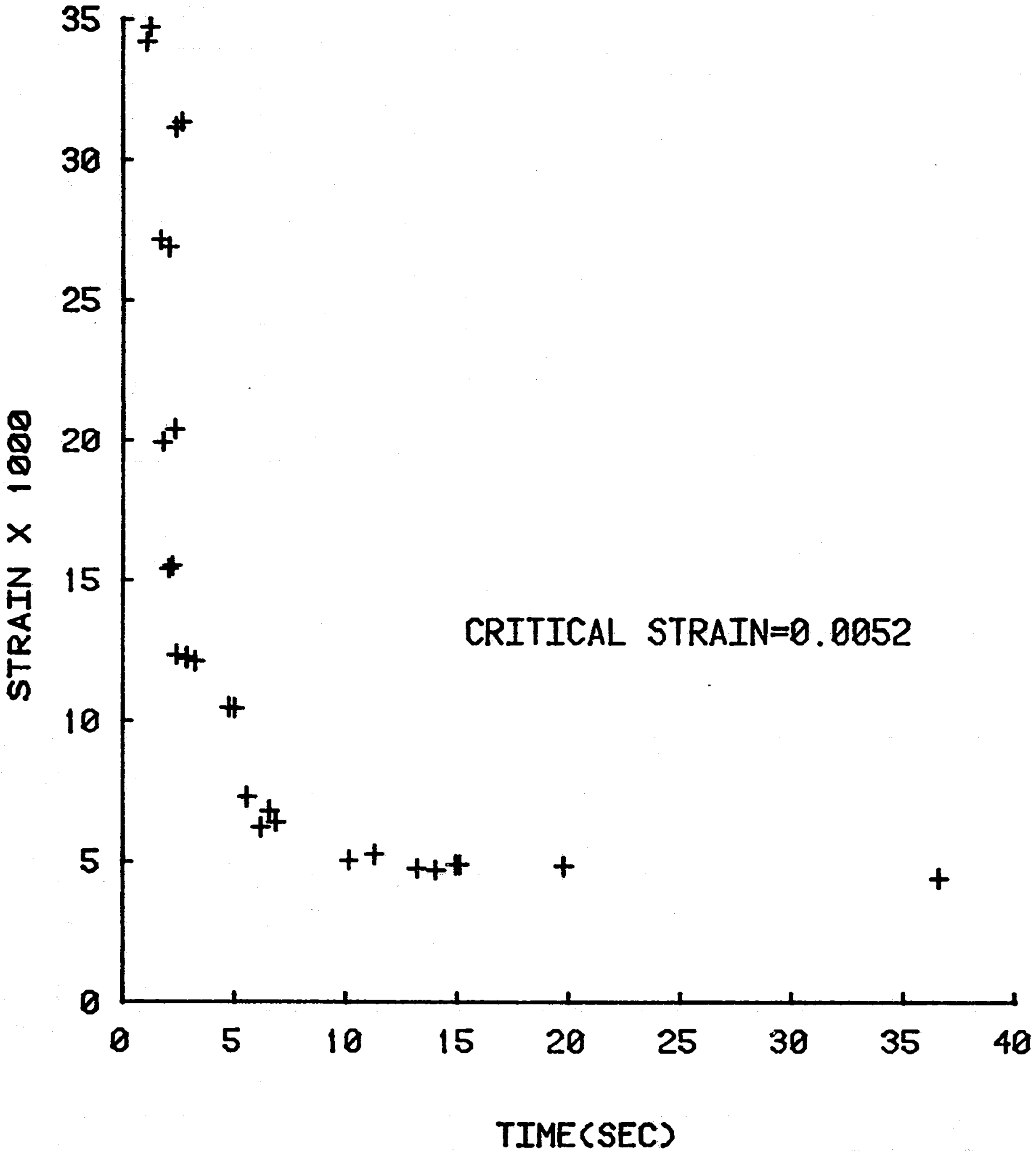

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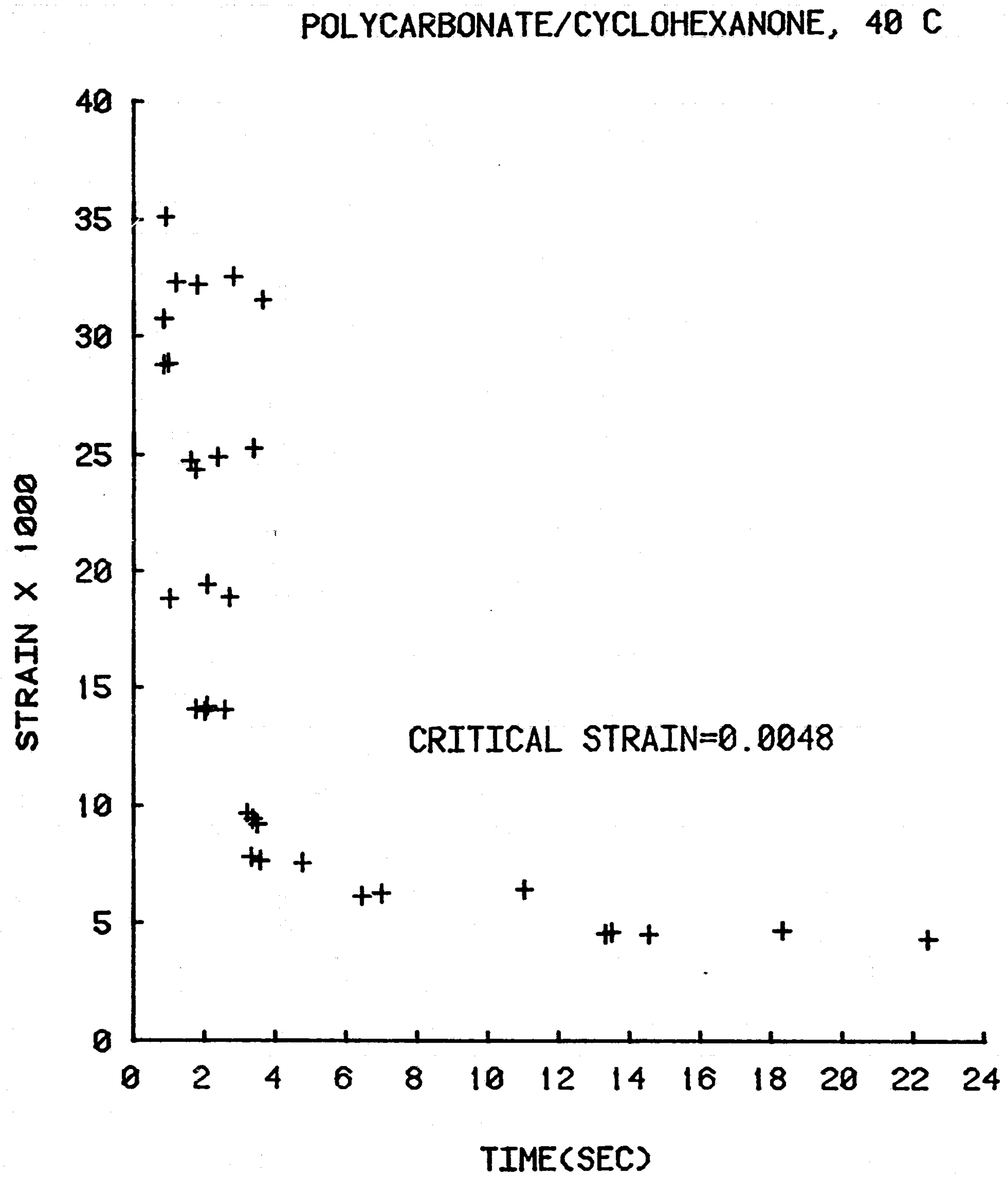
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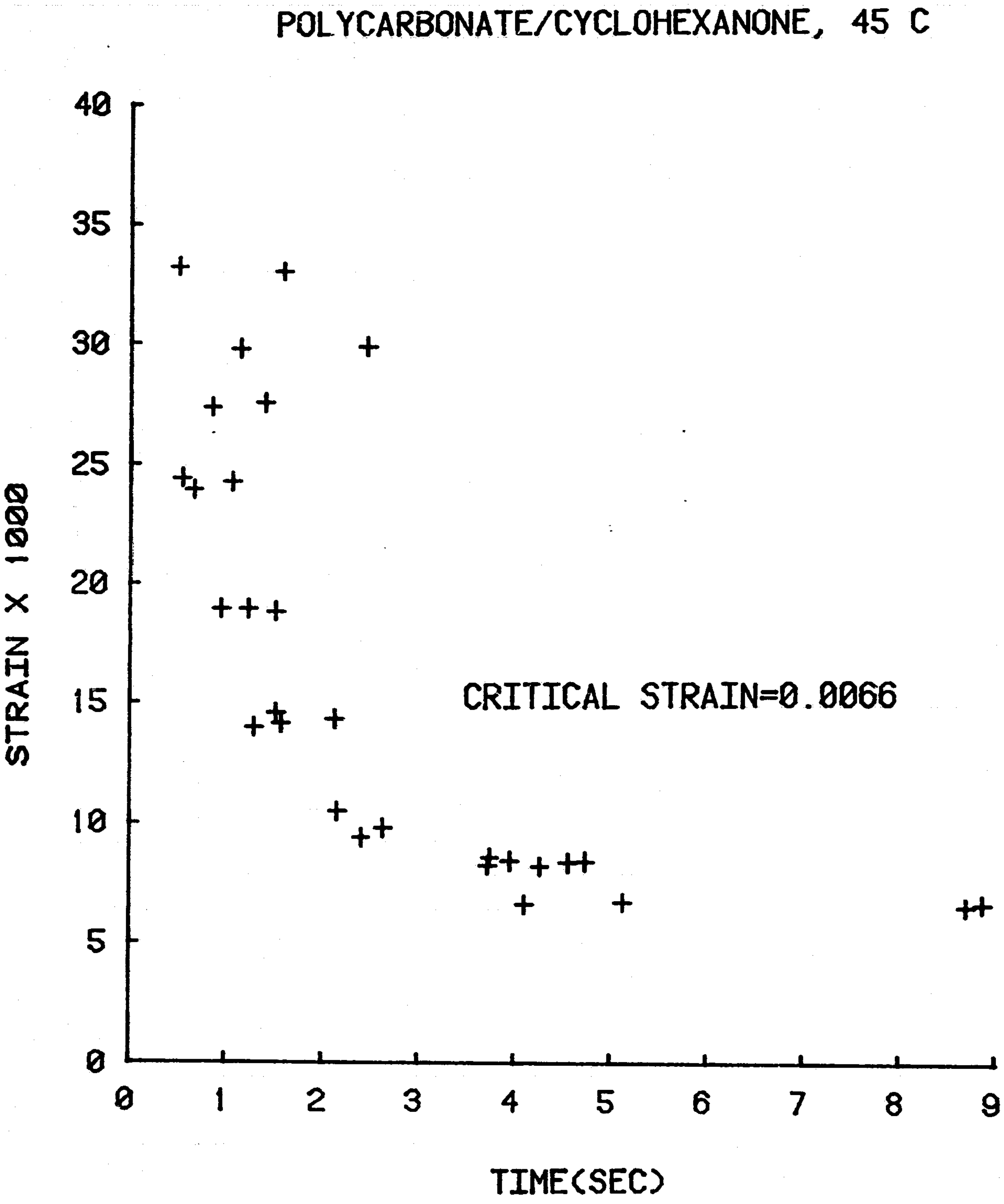
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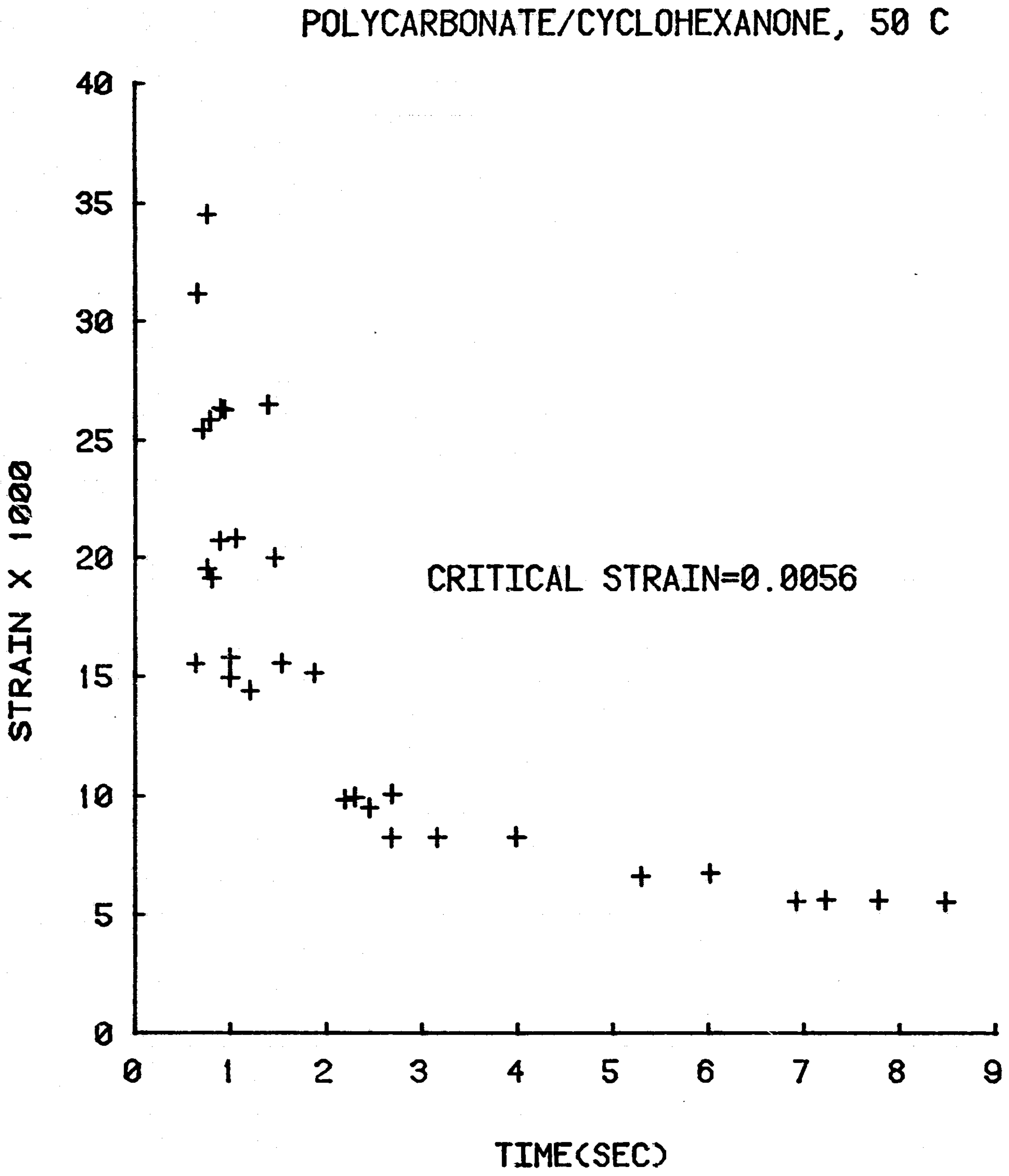
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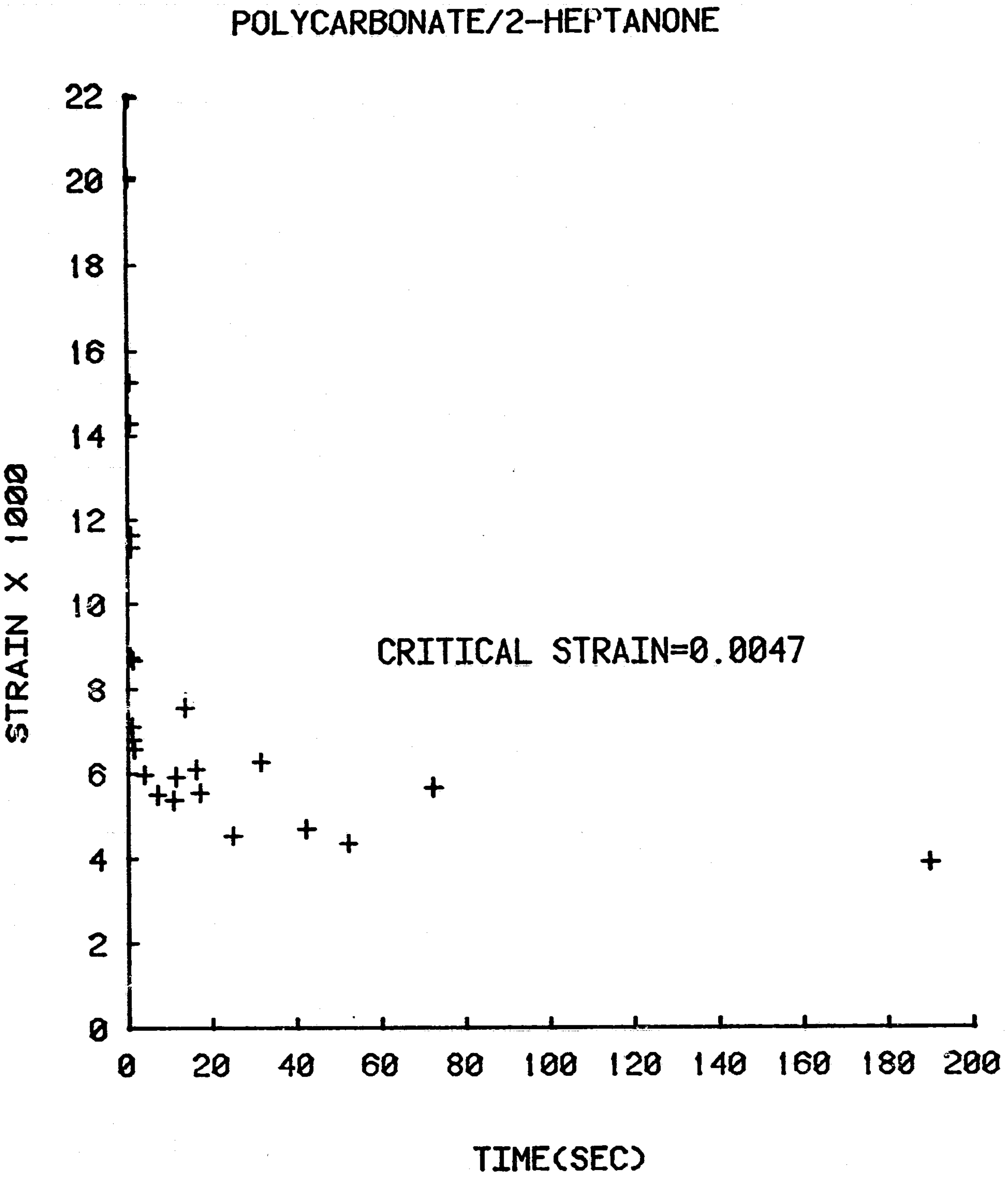
TIME(SEC)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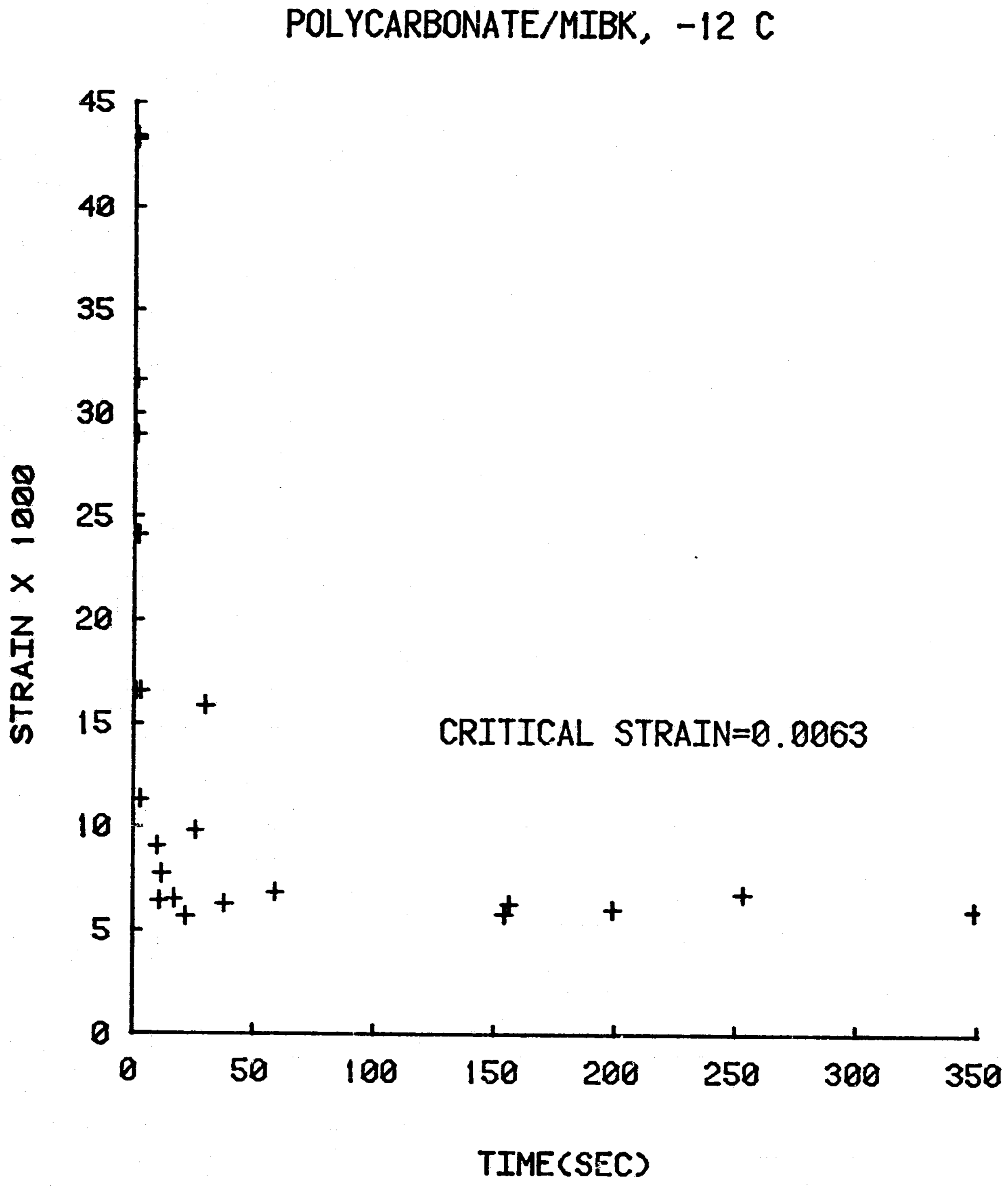
TIME(SEC)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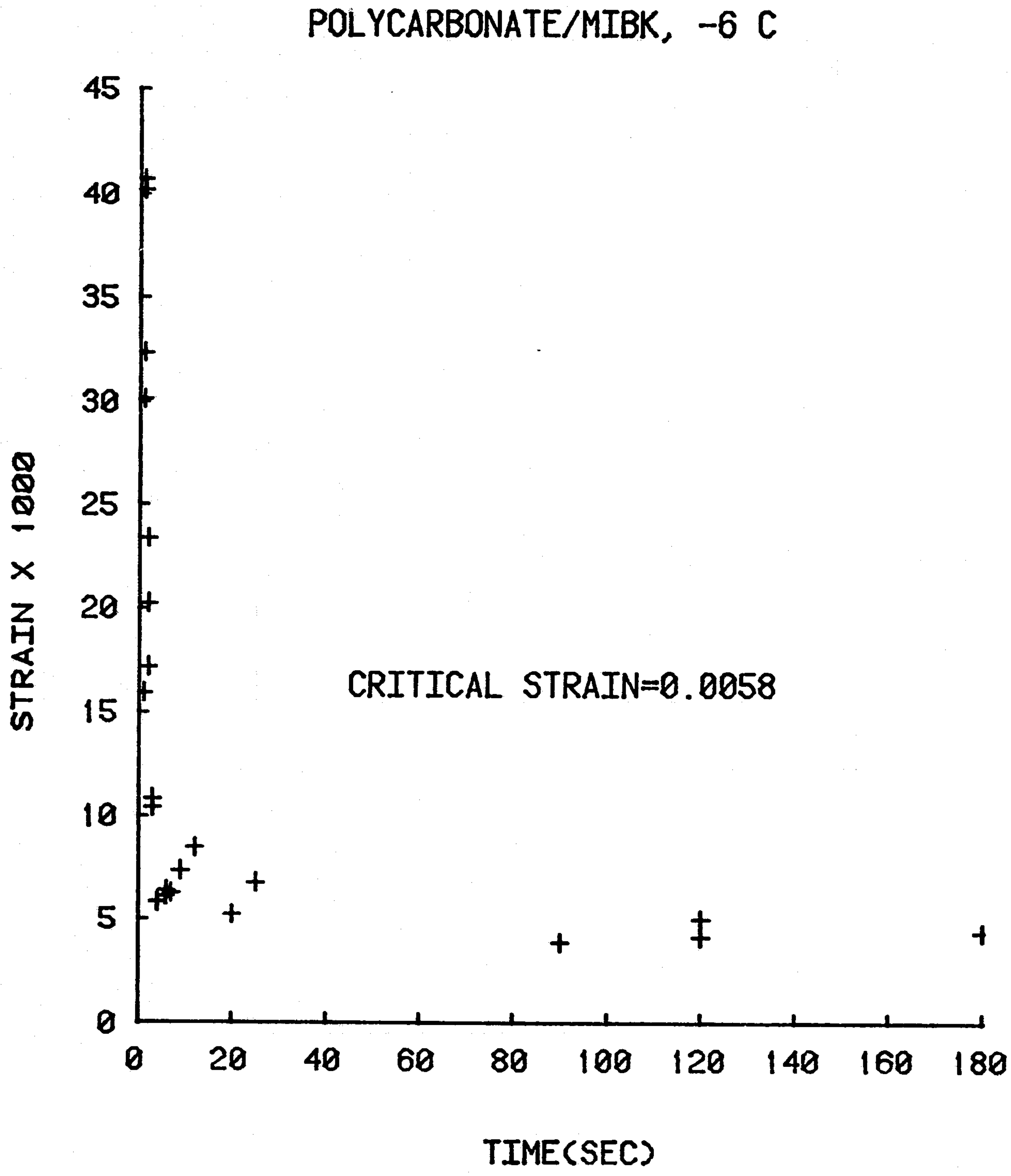
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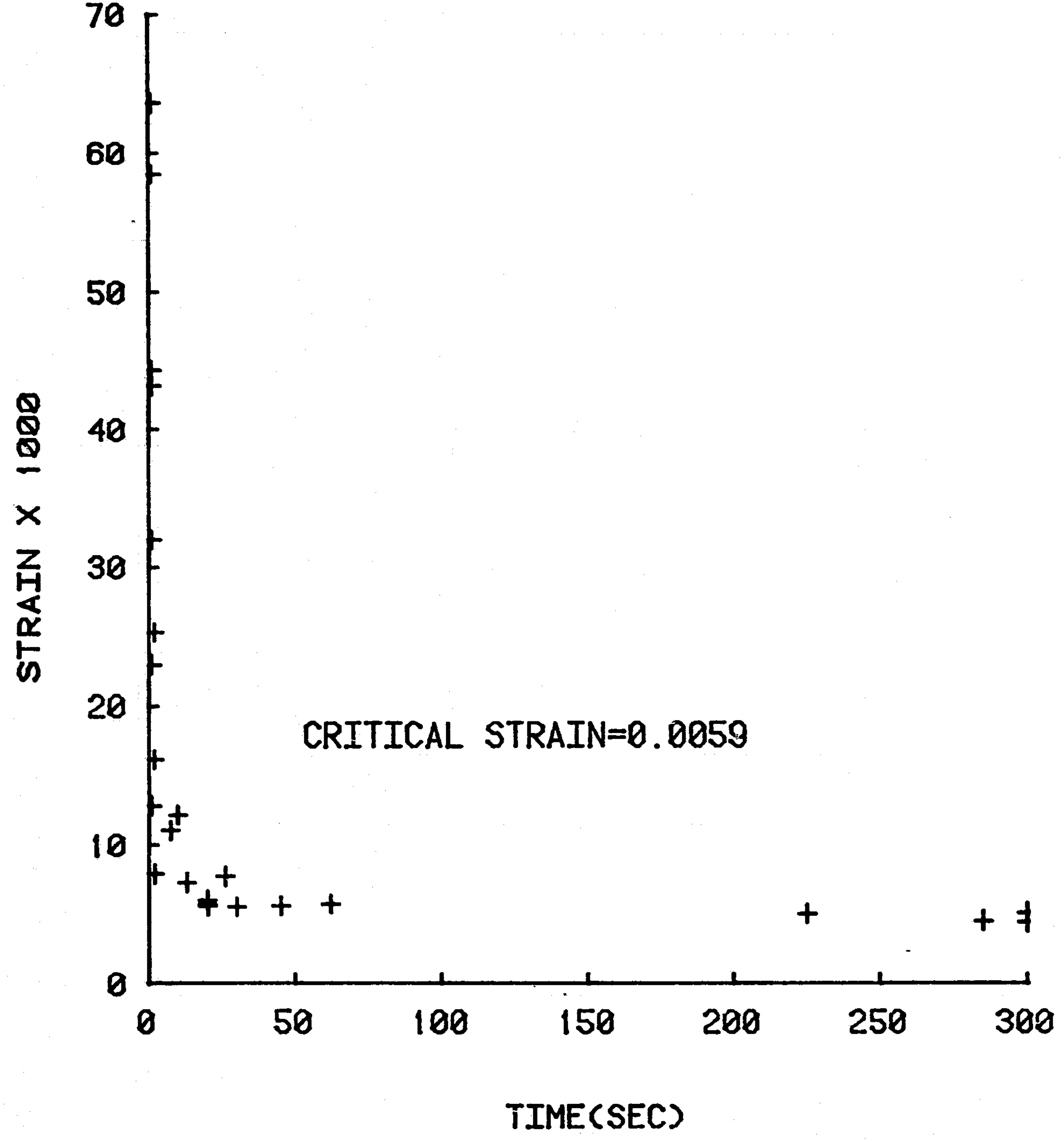

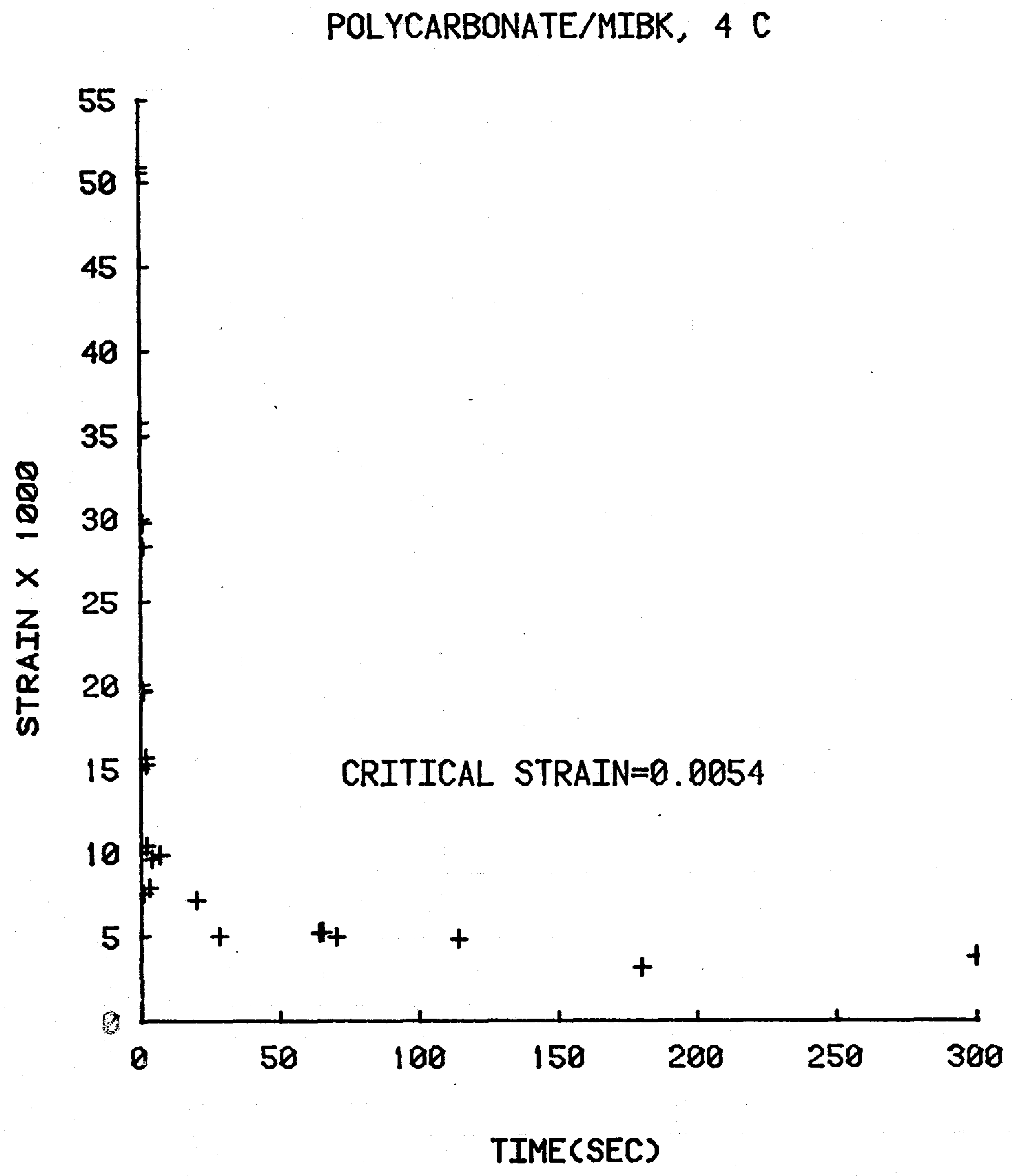
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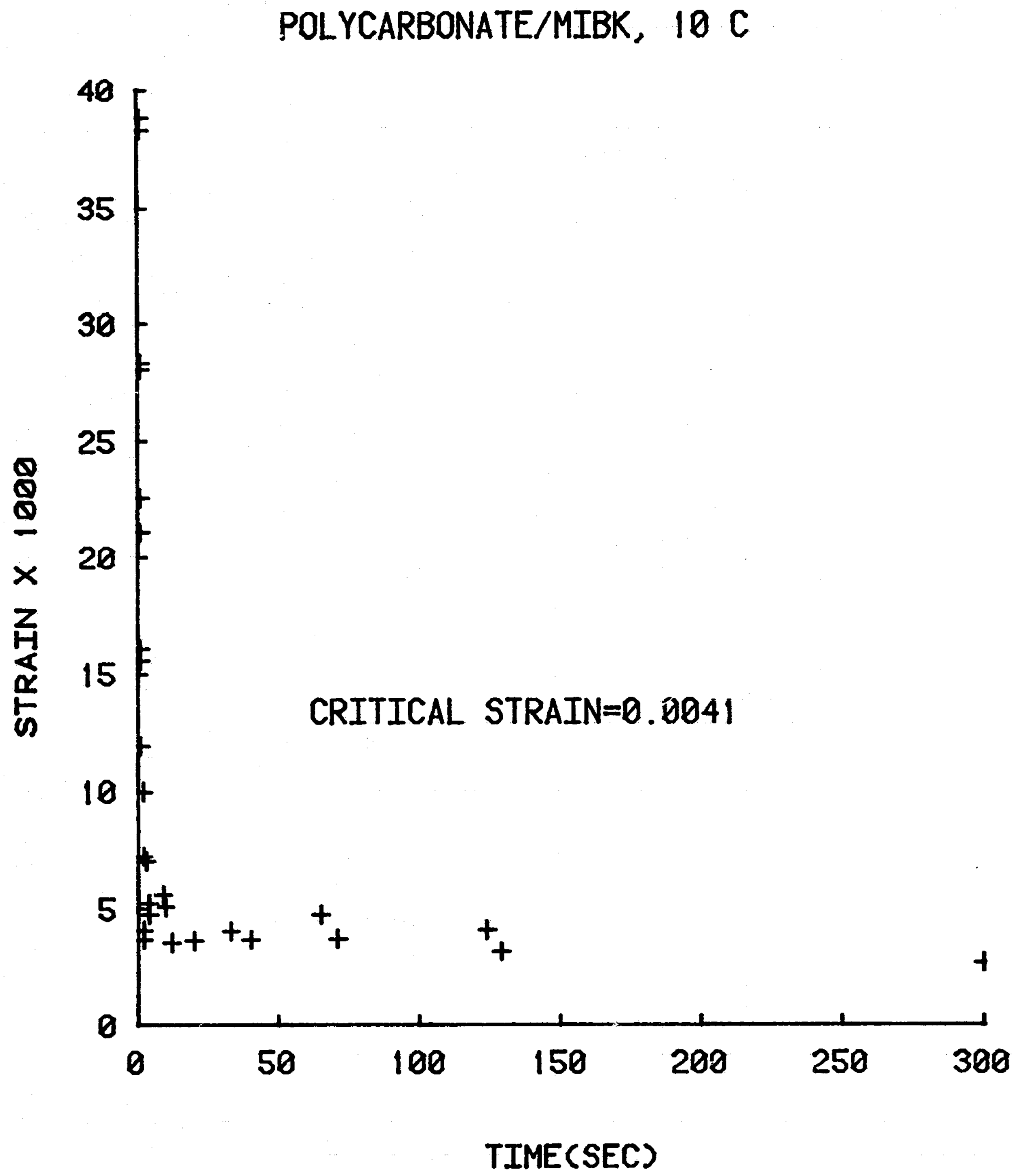
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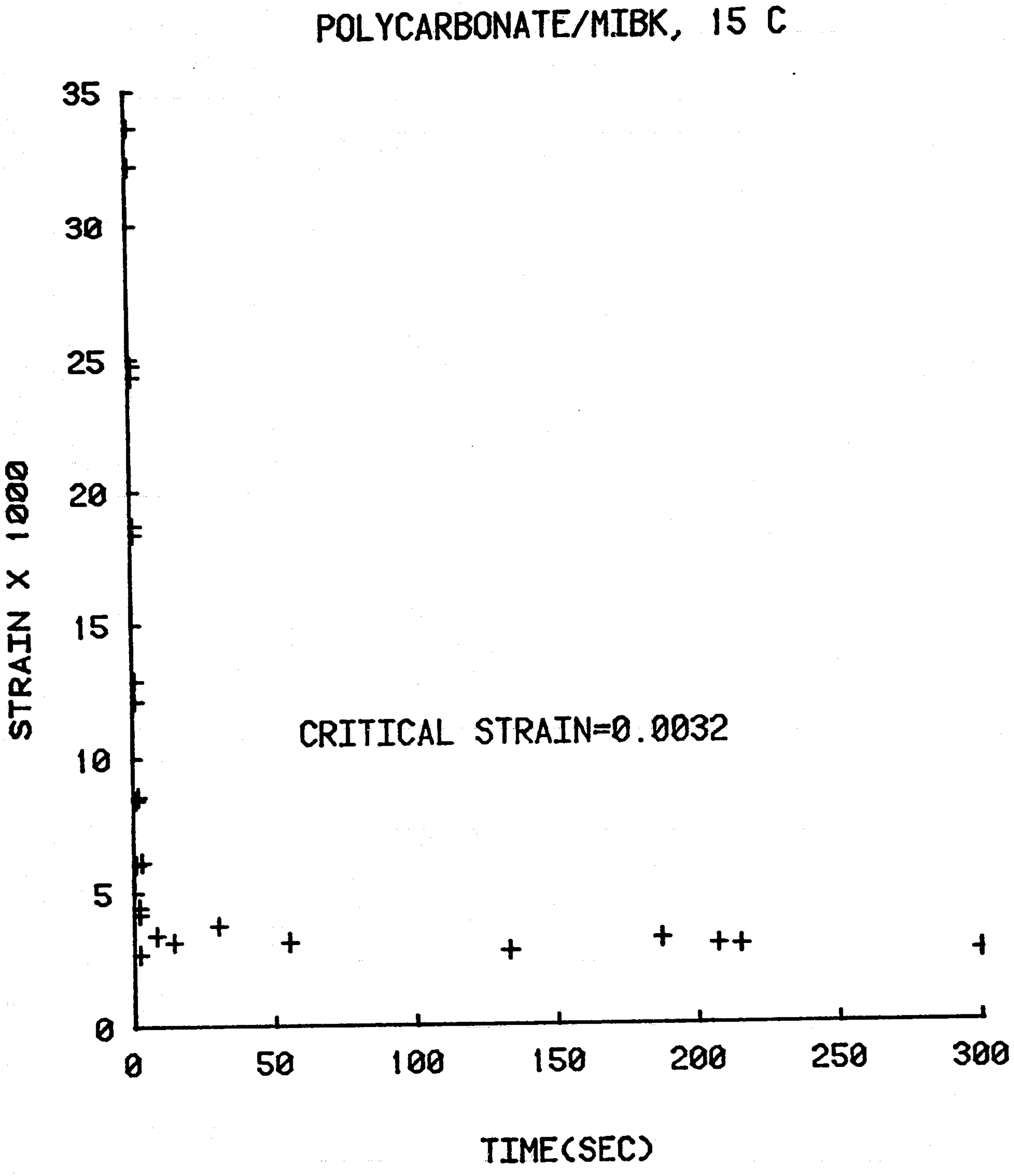POLYCARBONATE/MIBK, 15 C
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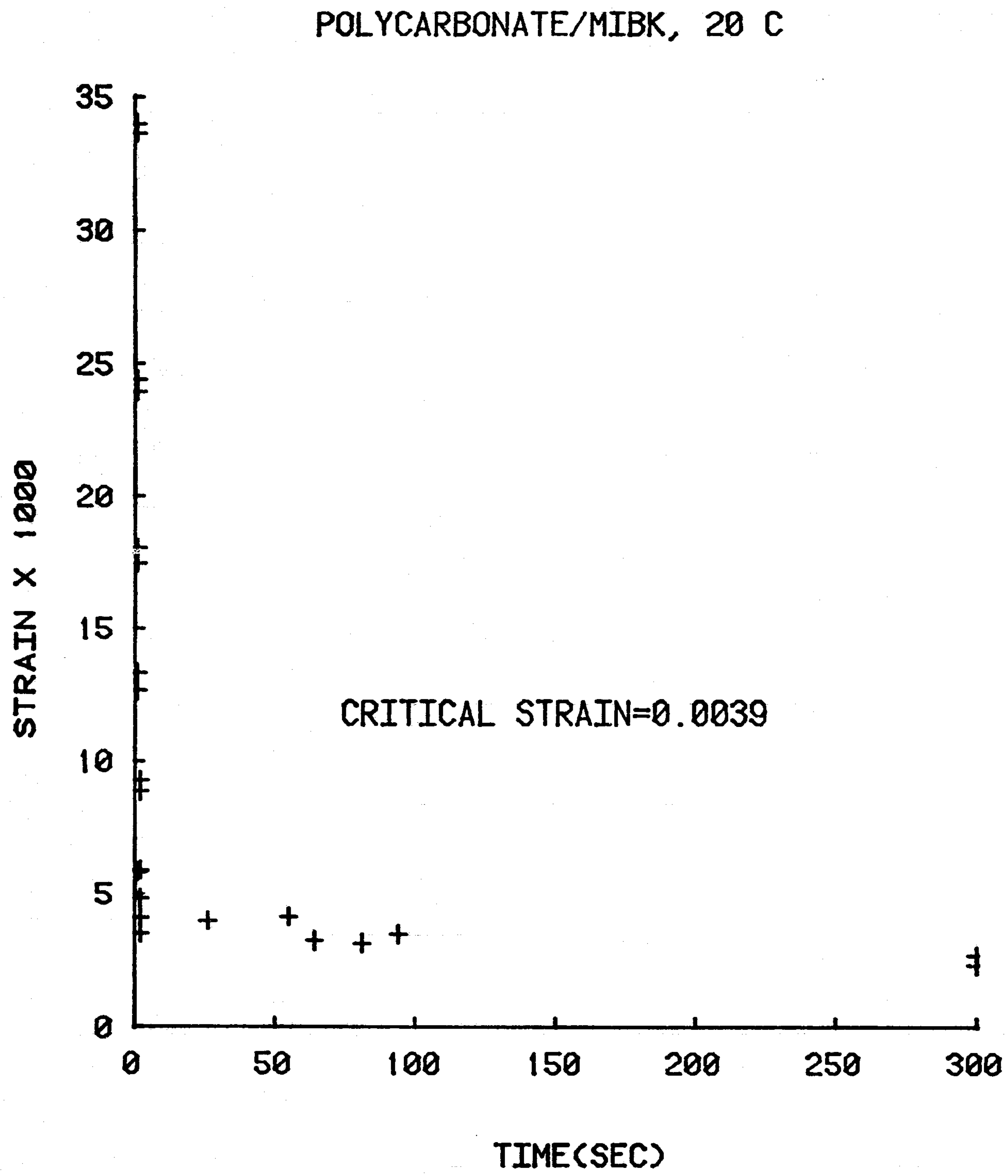
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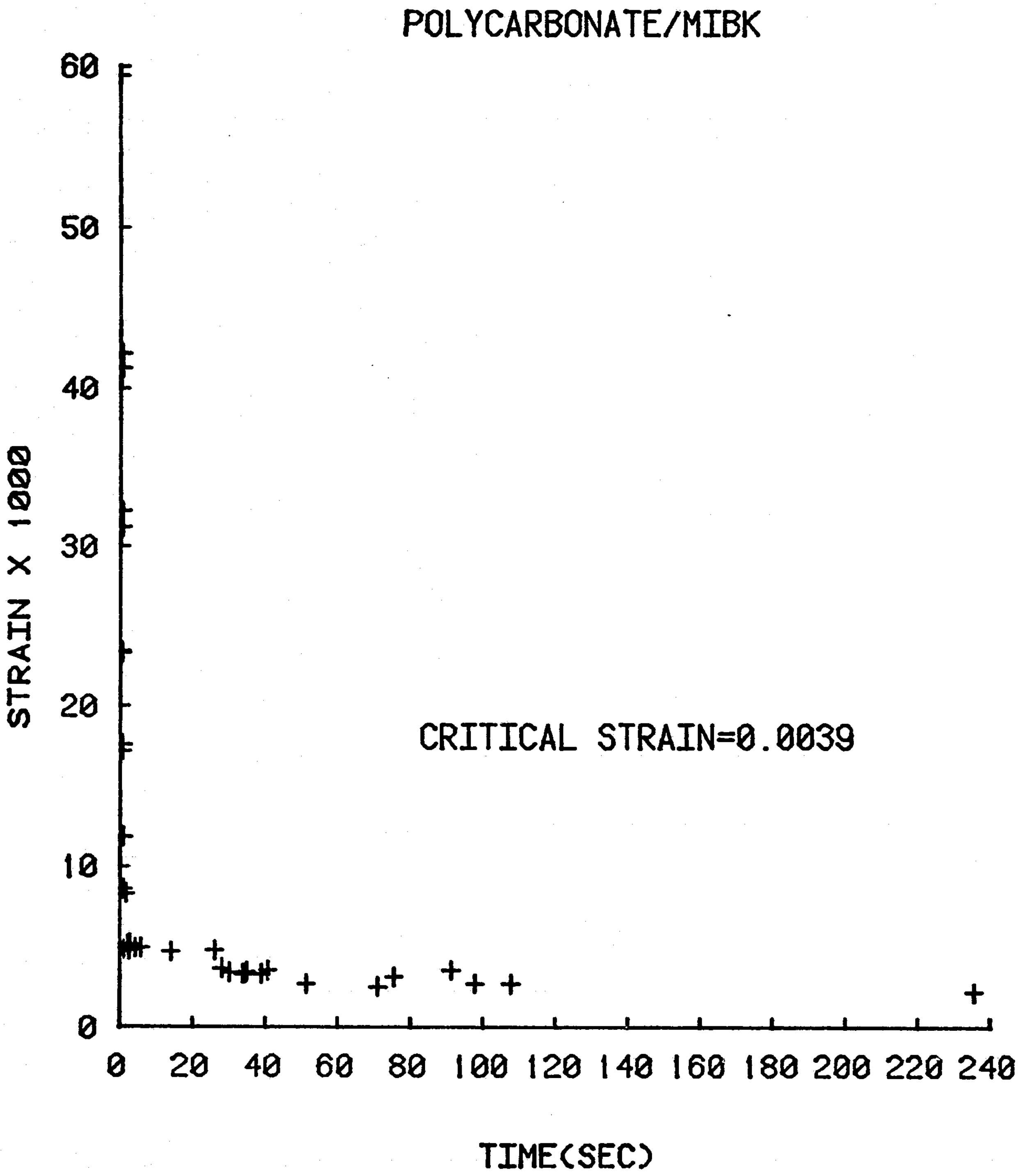
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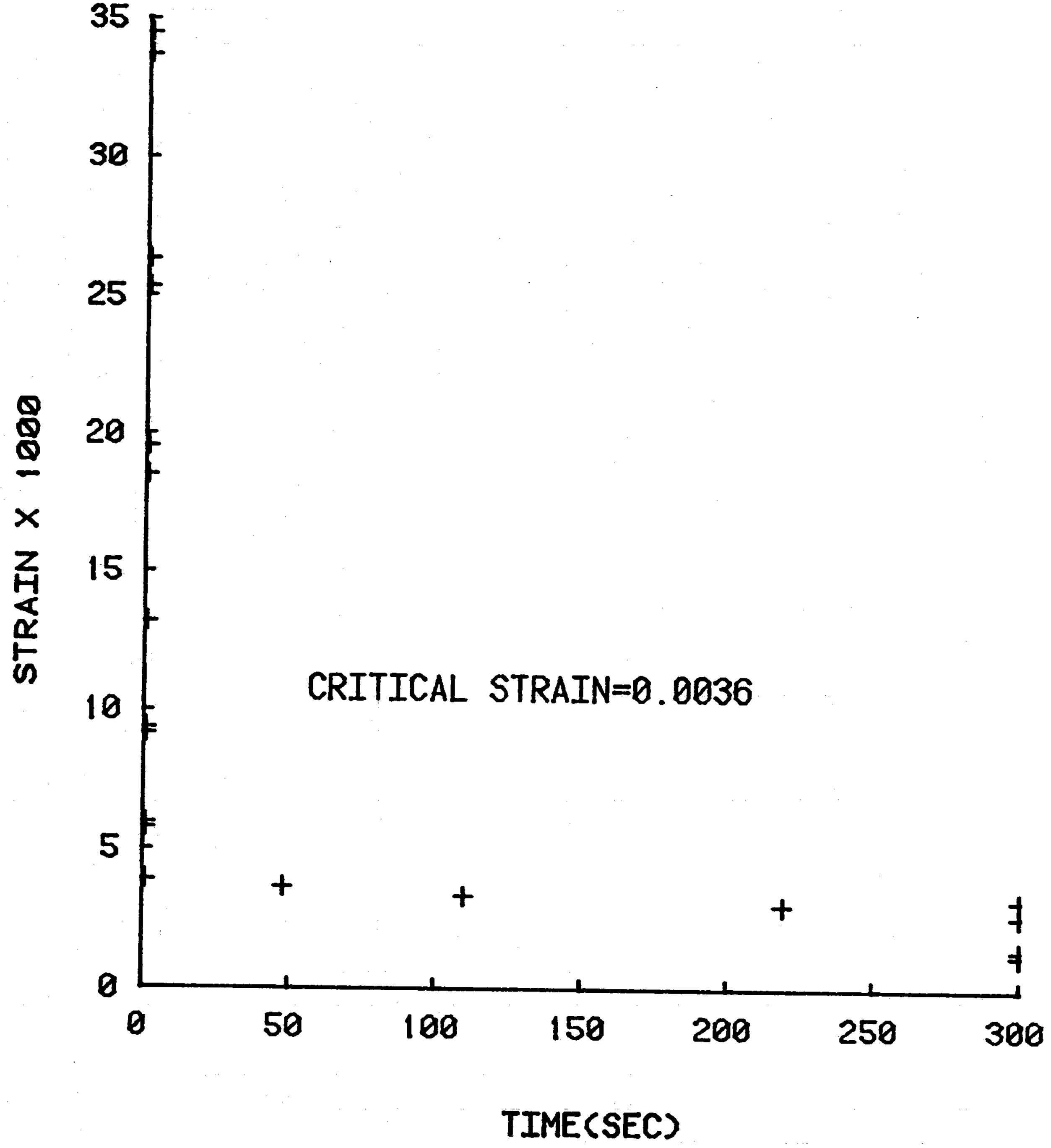
TIME(SEC)



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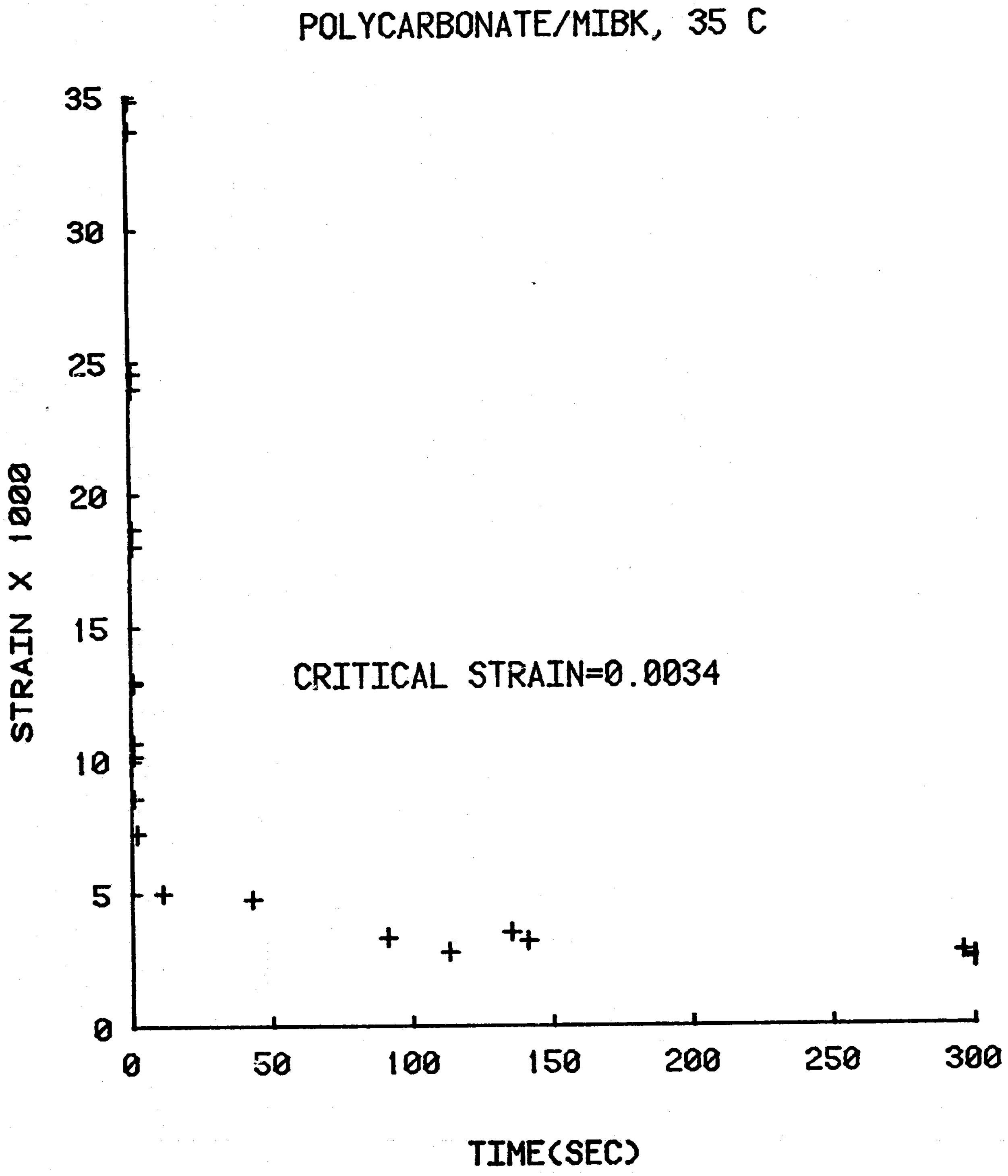POLYCARBONATE/MIBK, 35 C
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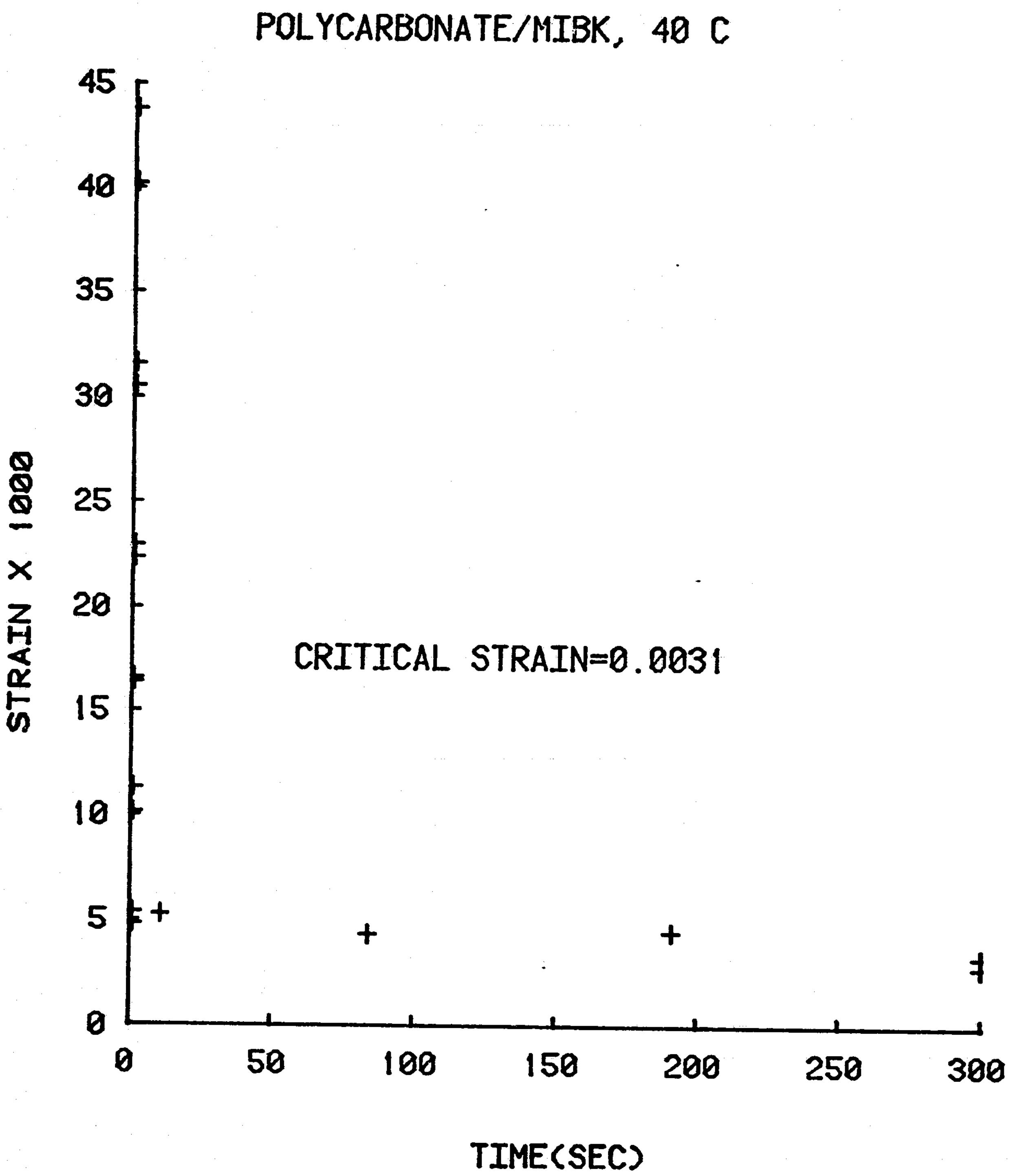
TIME(SEC)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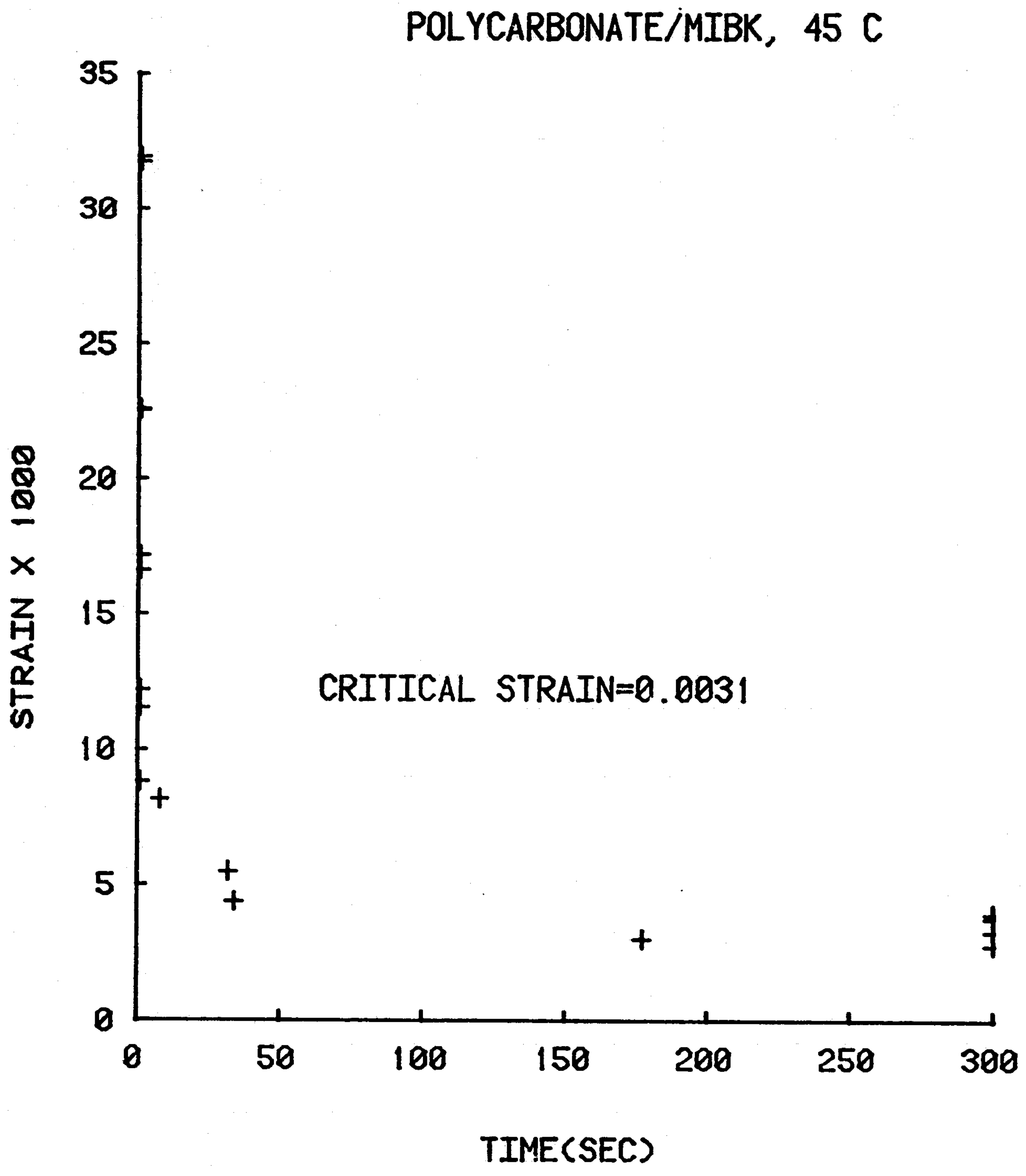
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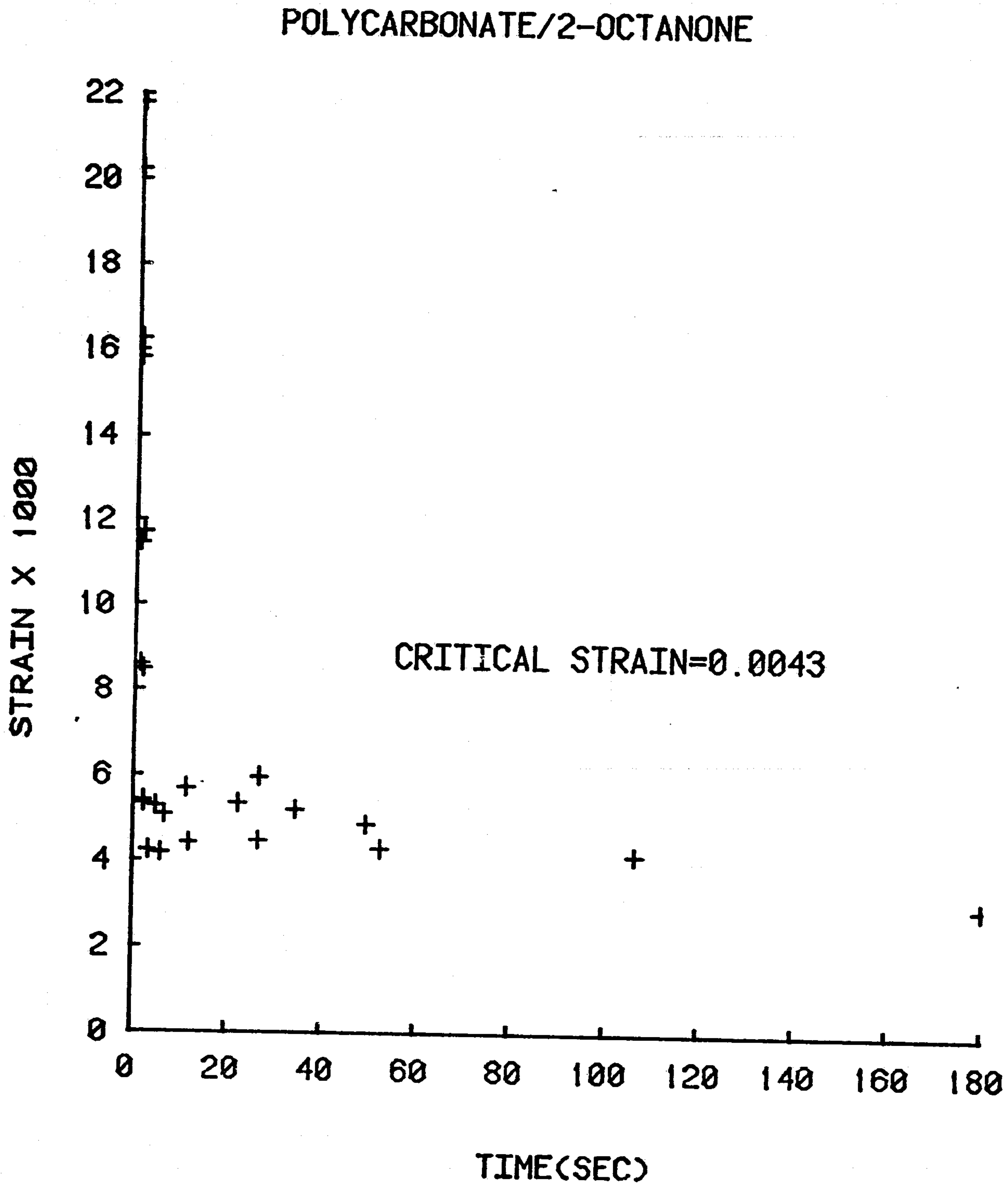POLYCARBONATE/2-OCTANONE
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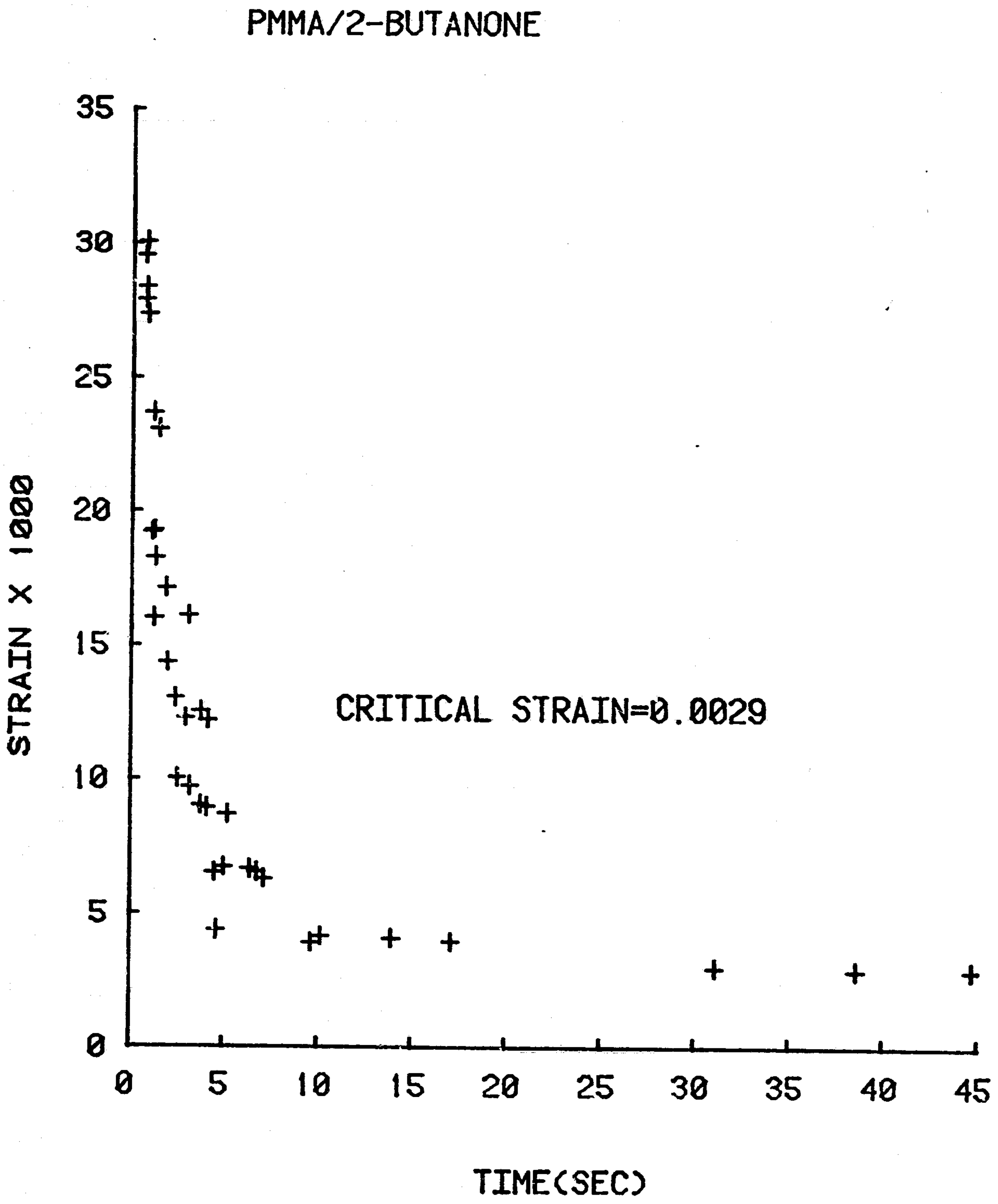
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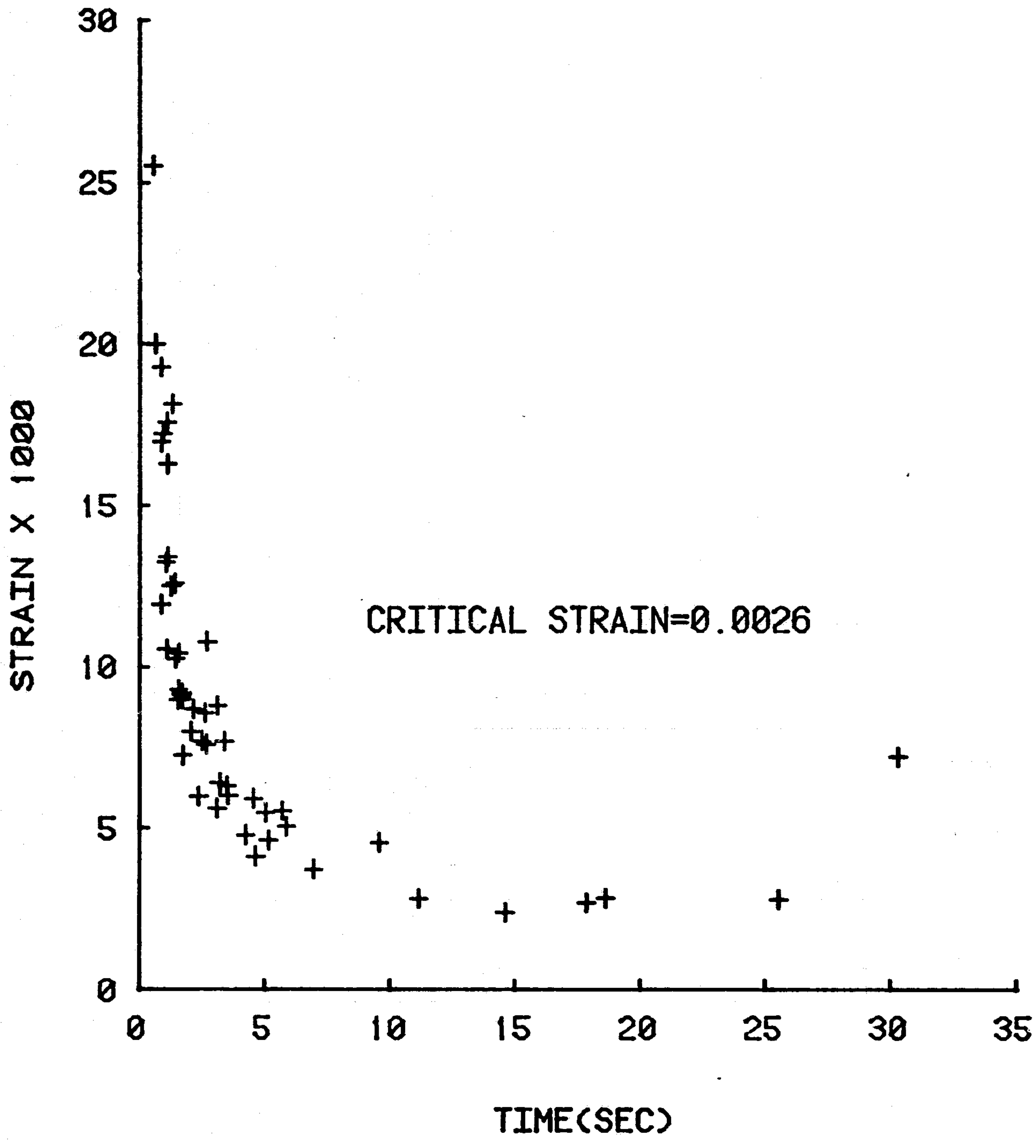
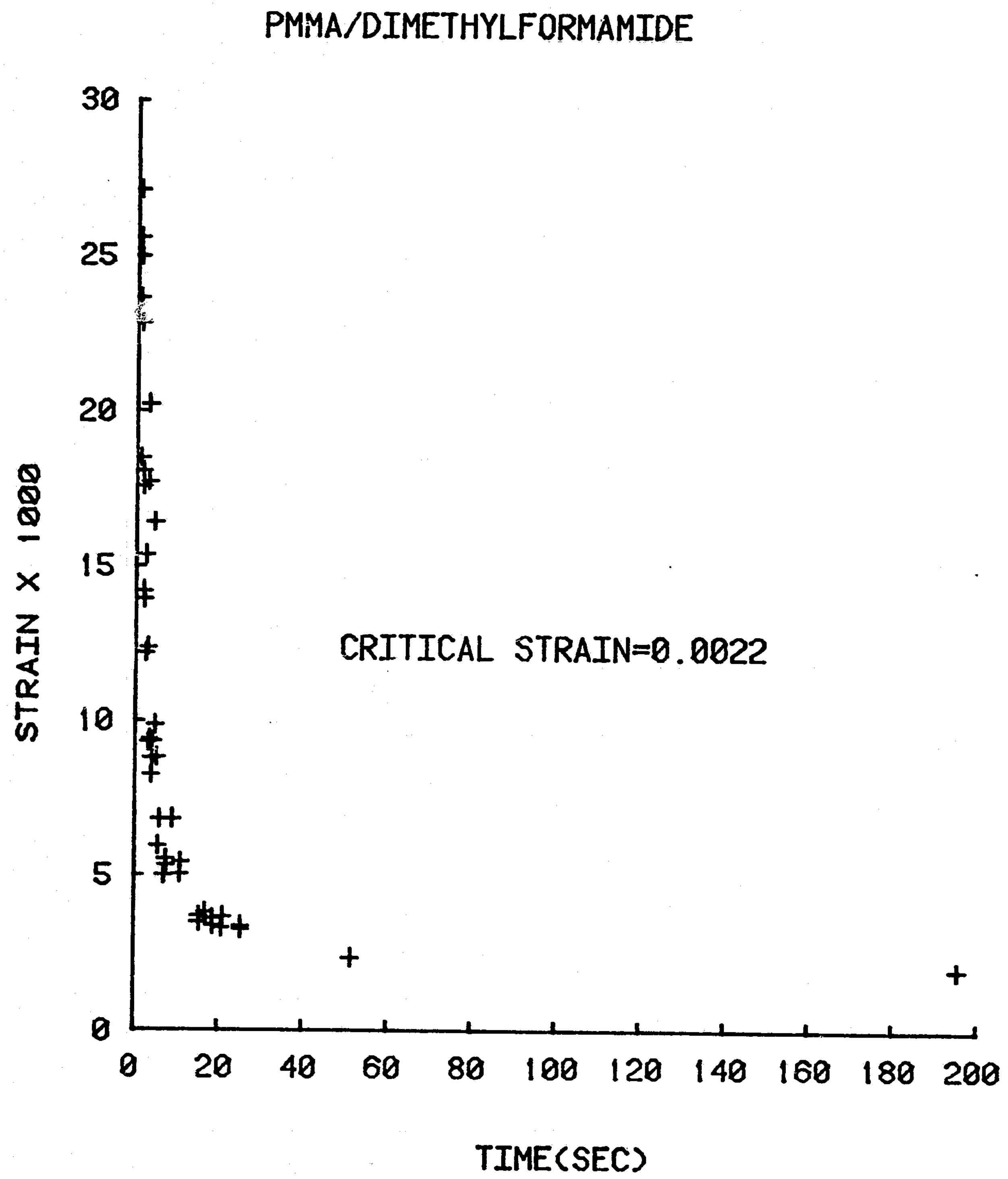
PMMA/ETHYLENE DICHLORIDE

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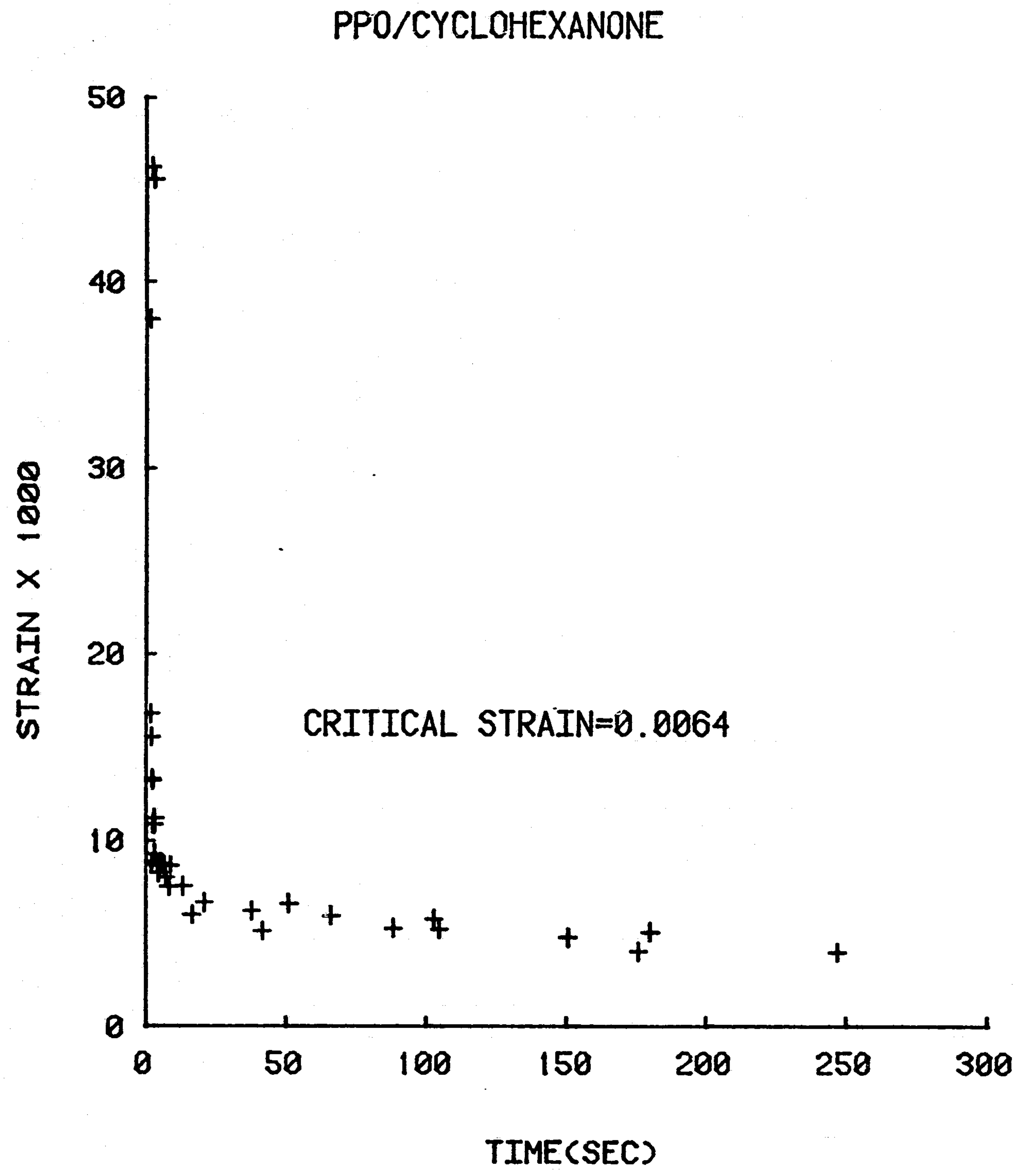
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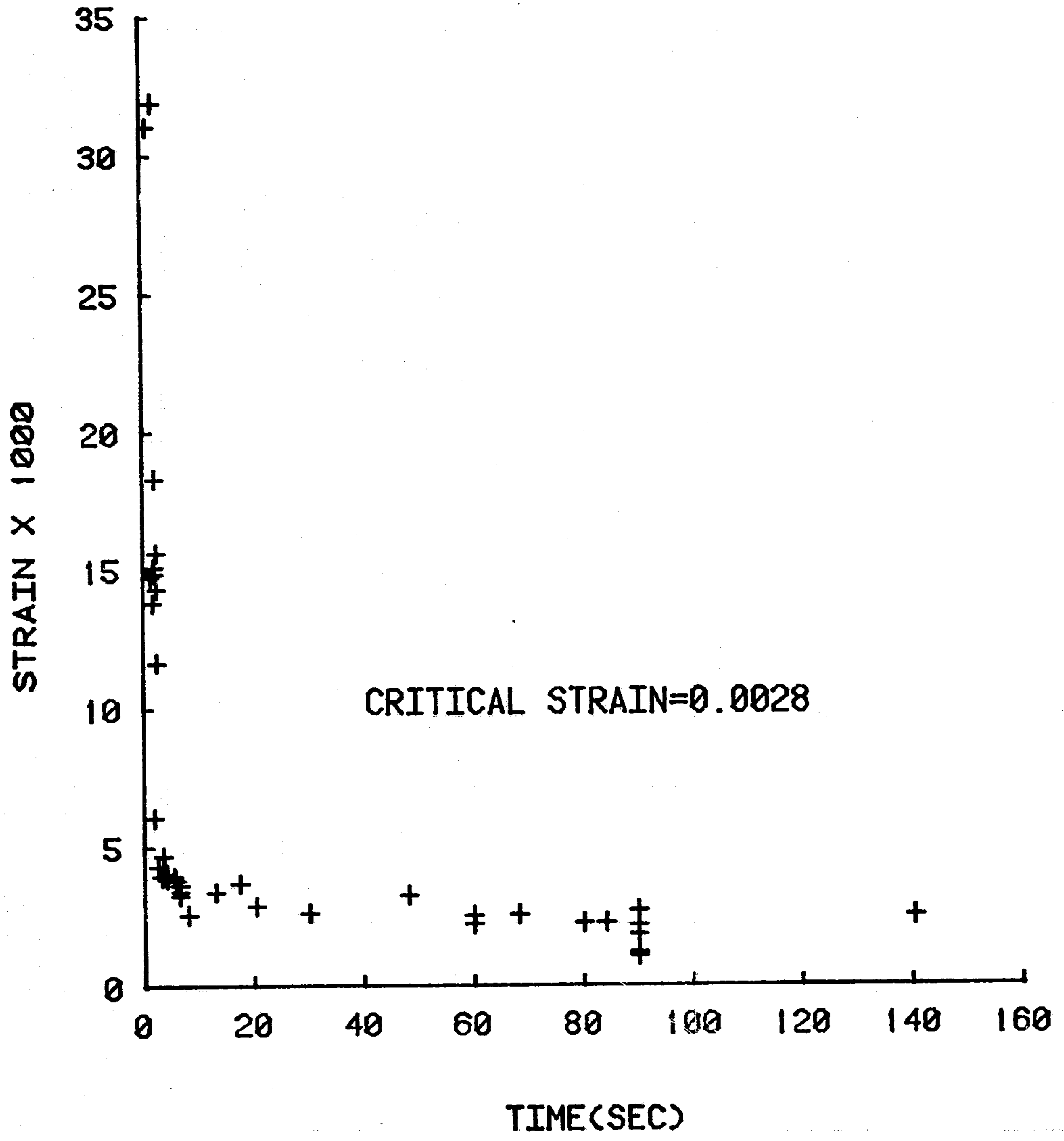
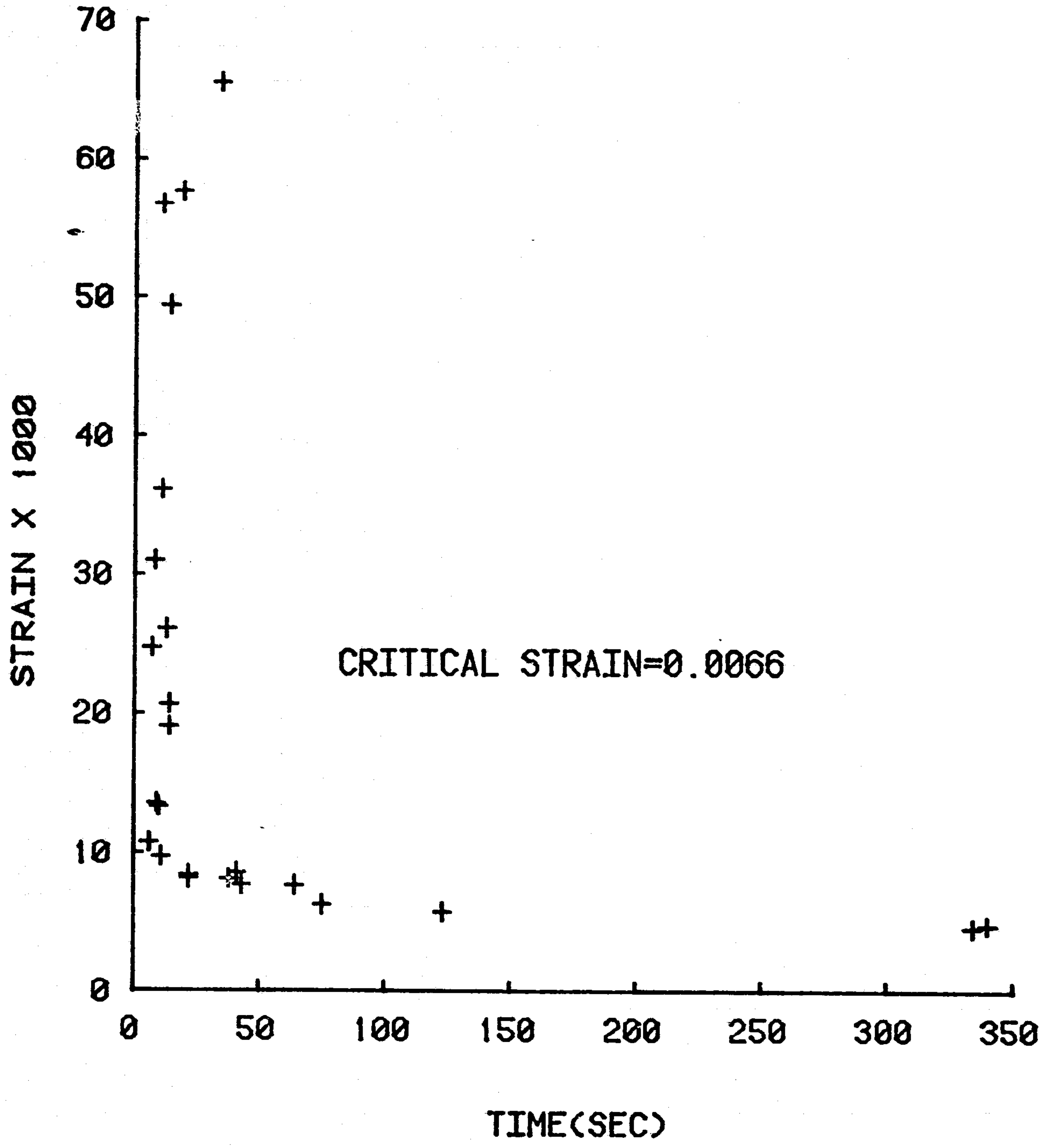
300

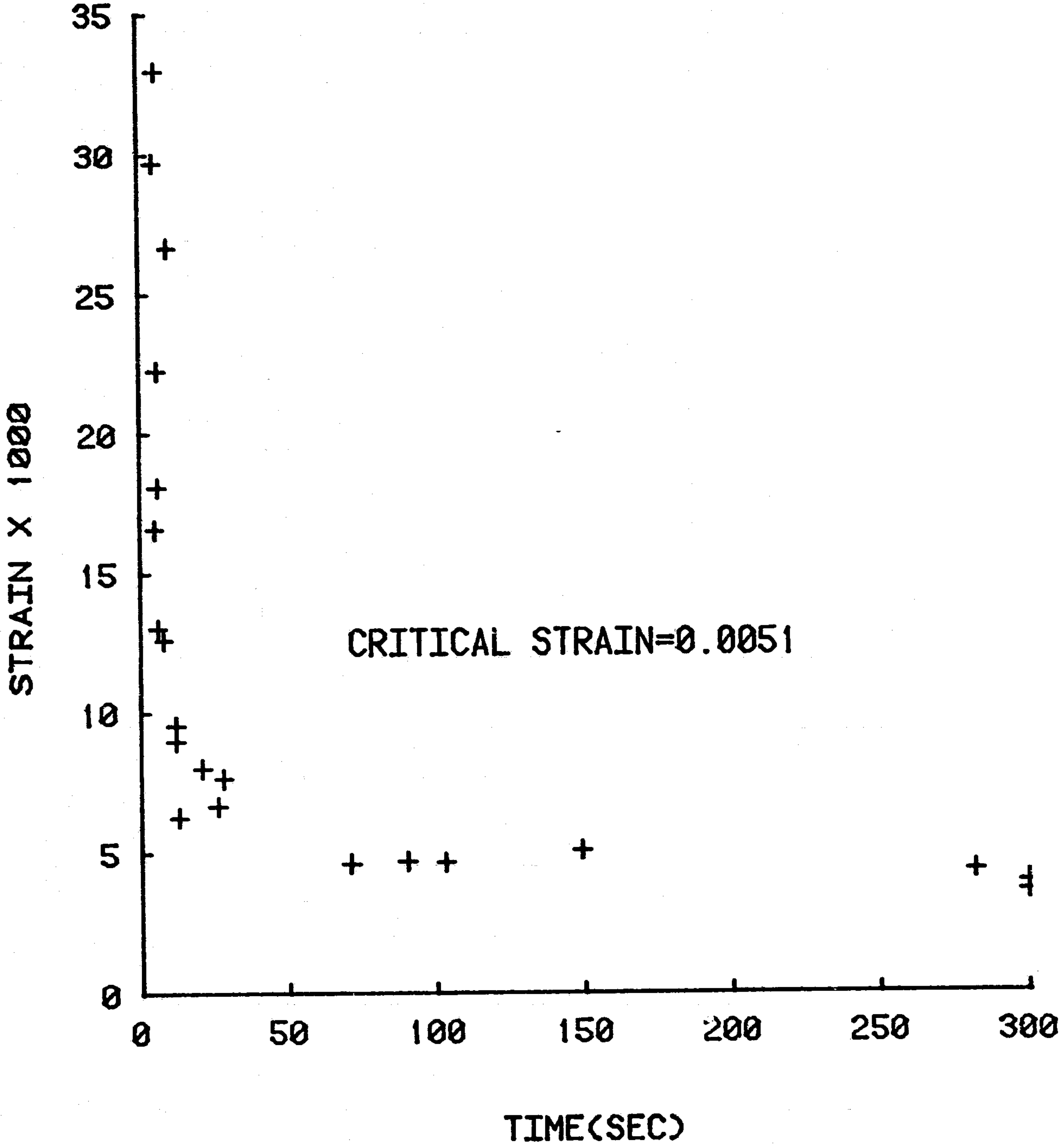


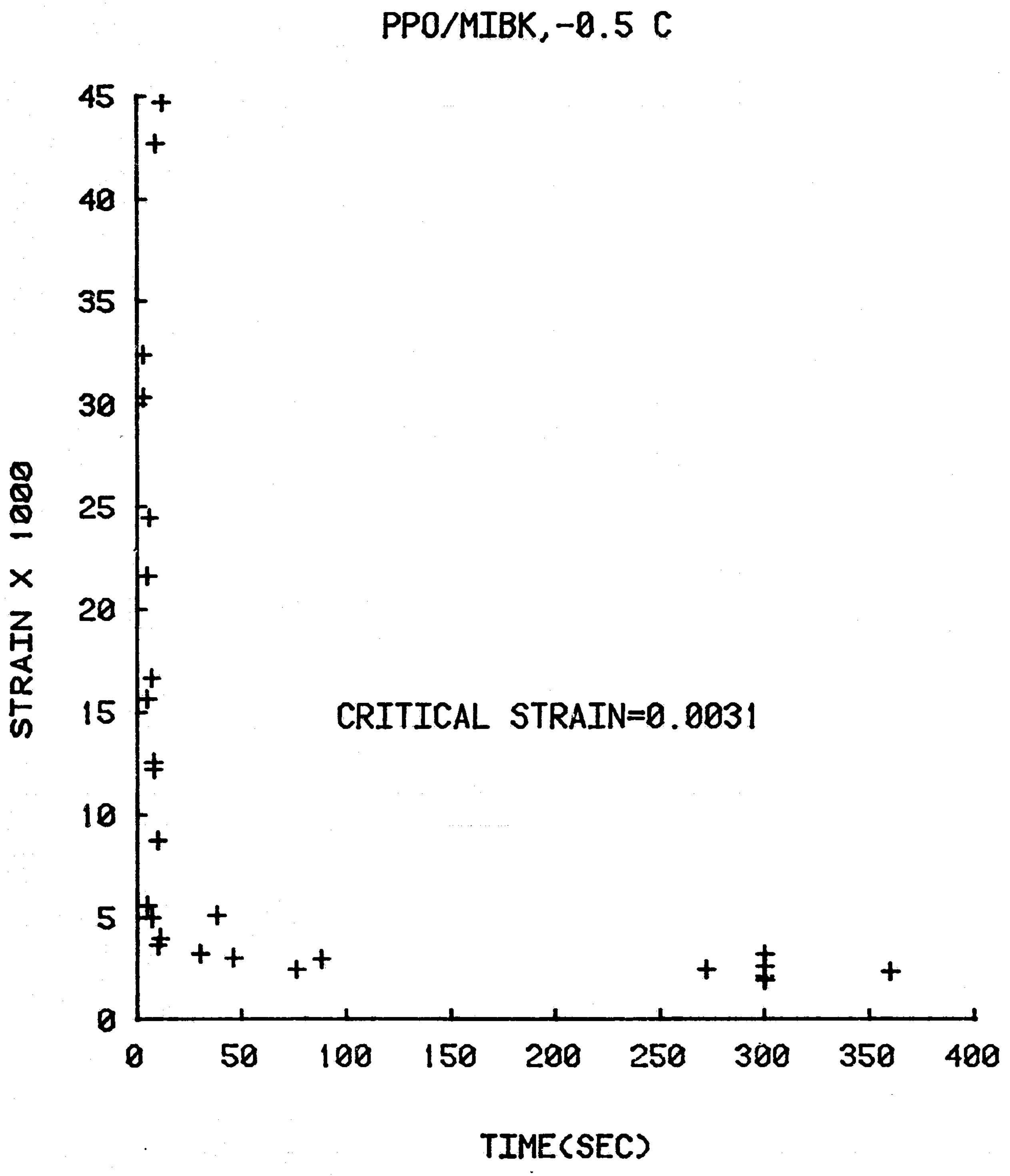
PPO/METHYL ACETATE

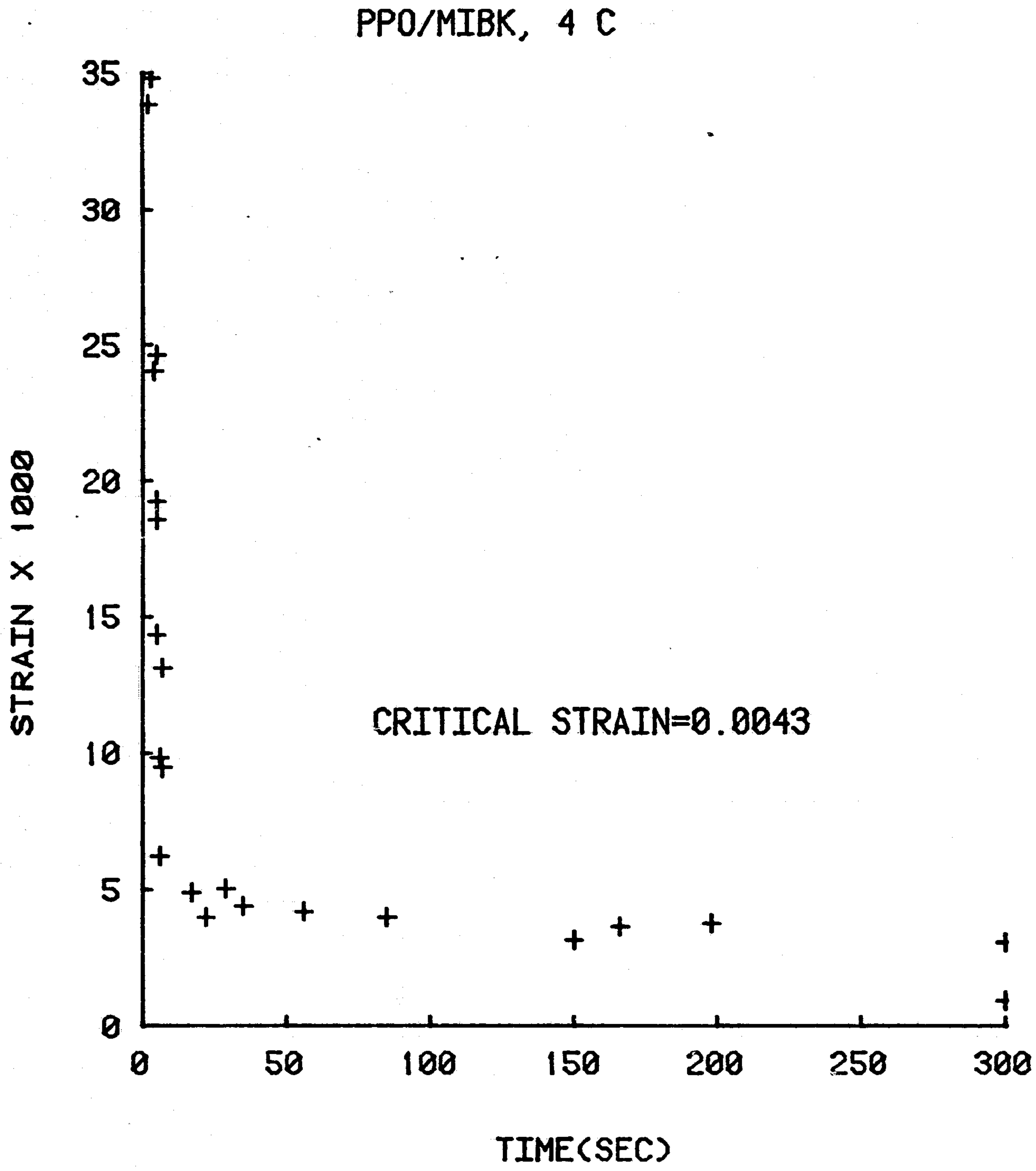
PPO/MIBK, -11 C

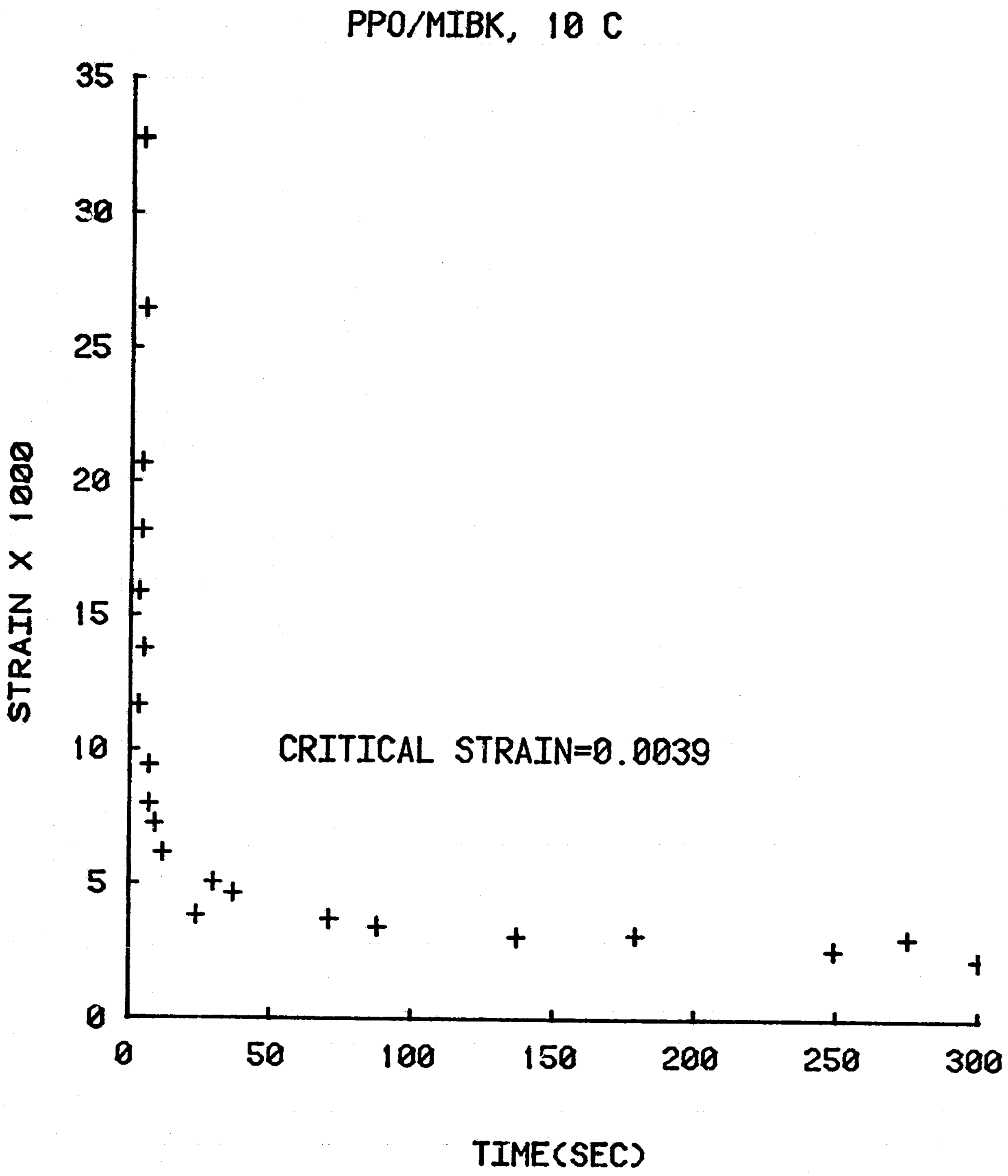

STRAIN X 1000
70
60
50
40
30
20
10
0
CRITICAL STRAIN=0.0066
0
50
100
150
200
250
300
350
TIME(SEC)

PPO/MIBK, -5 C

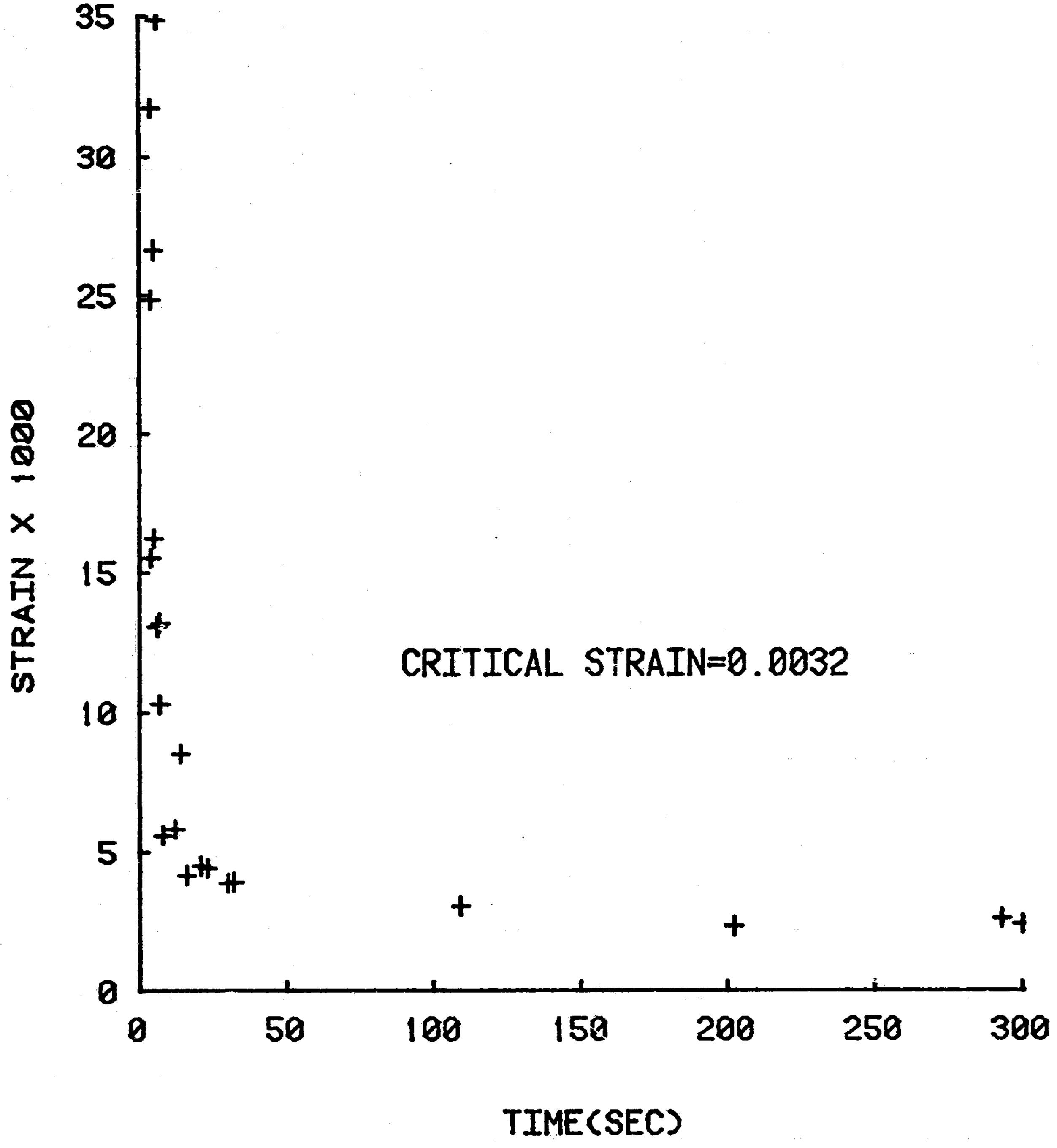

STRAIN X 1000
35
30
25
20
15
10
5
0
CRITICAL STRAIN=0.0051
0
50
100
150
200
250
300
TIME(SEC)

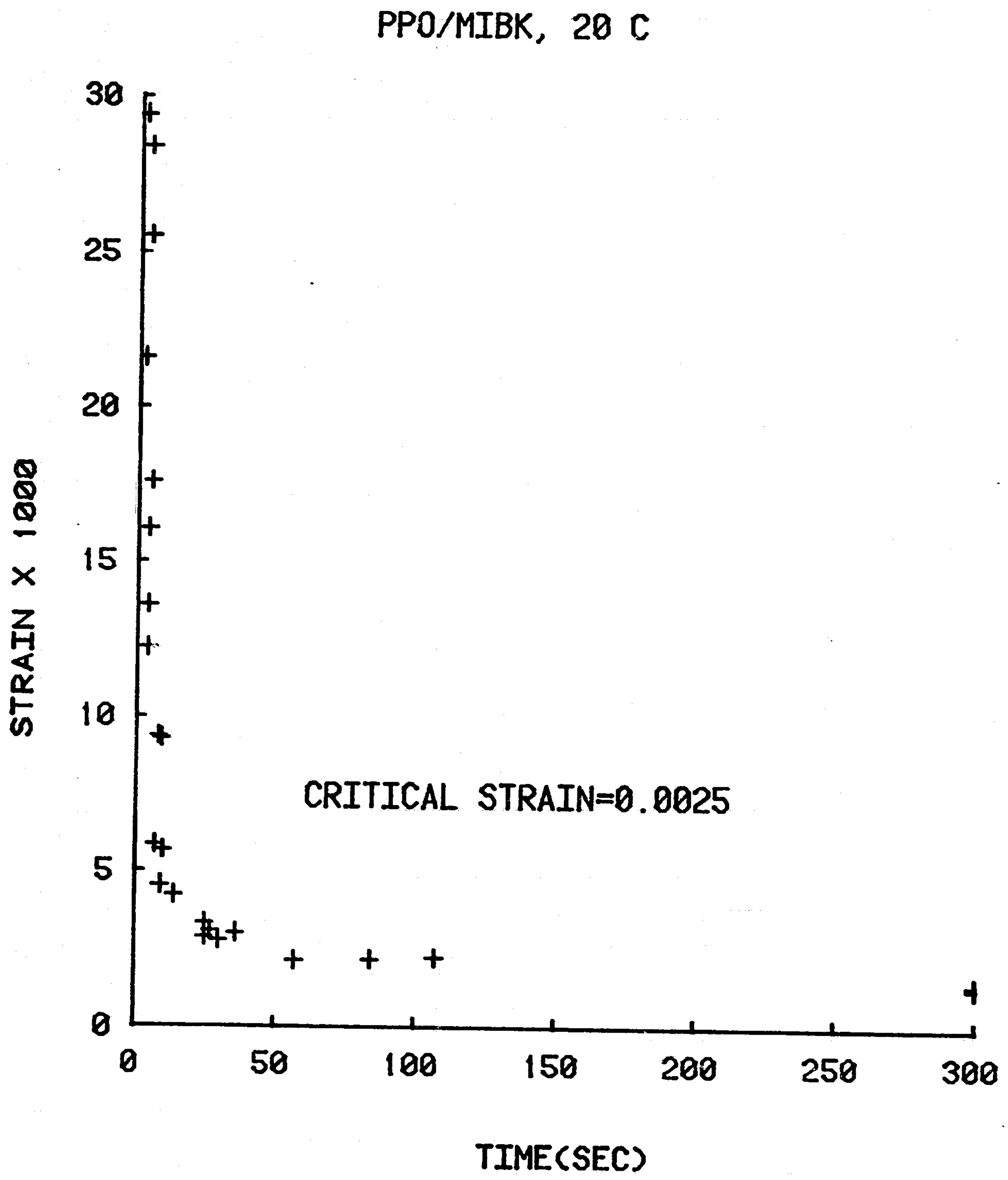

PPO/MIBK,-0.5 C
STRAIN X 1000
45
40
35
30
25
20
15
10
5
0
CRITICAL STRAIN=0.0031
0
50
100
150
200
250
300
350
400
TIME(SEC)


PPO/MIBK, 4 C
CRITICAL STRAIN=0.0043
STRAIN X 1000
0
5
10
15
20
25
30
35
TIME(SEC)
0
50
100
150
200
250
300

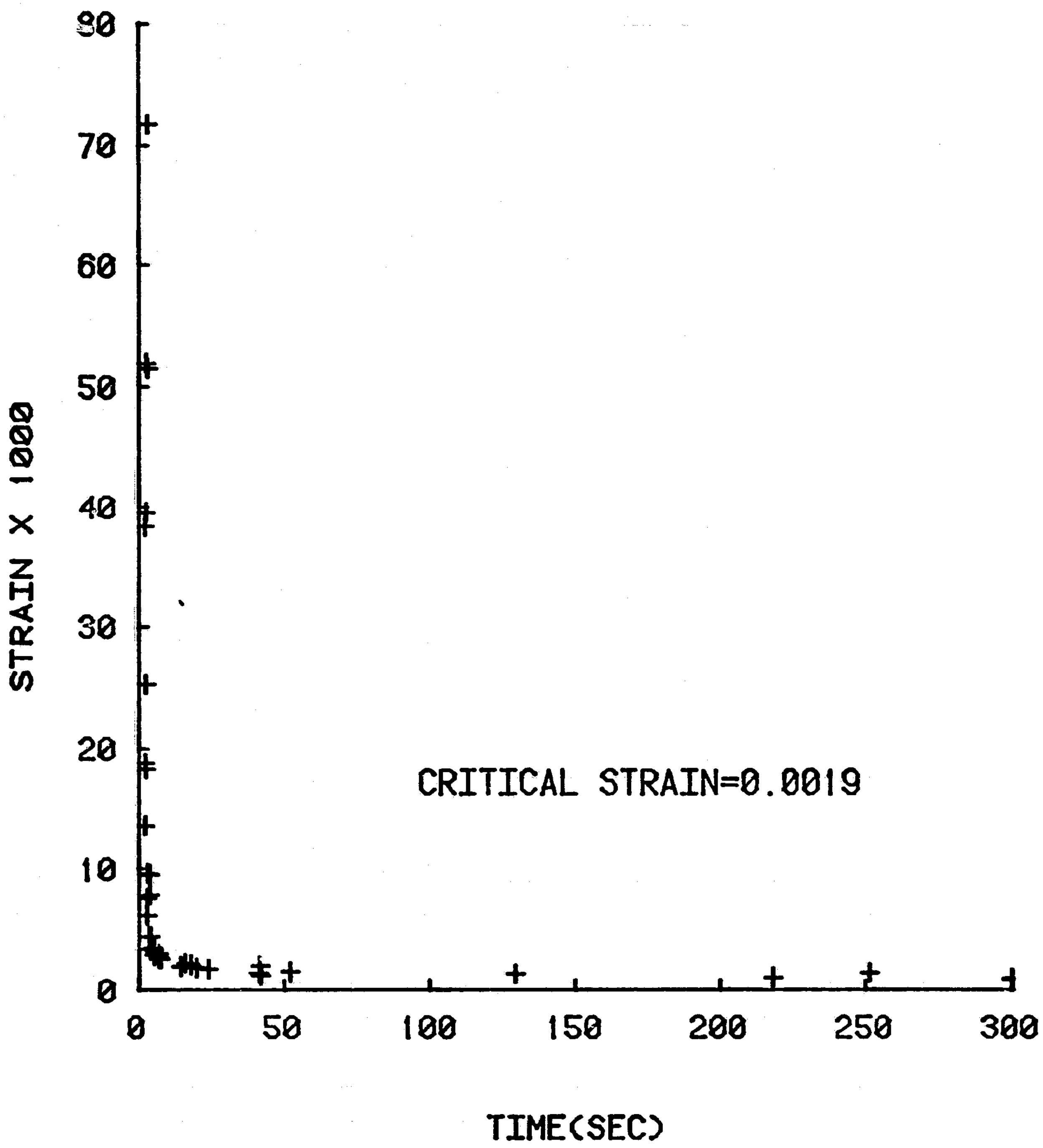

PPO/MIBK, 10 C
CRITICAL STRAIN=0.0039
STRAIN X 1000
0
5
10
15
20
25
30
35
TIME(SEC)
0
50
100
150
200
250
300

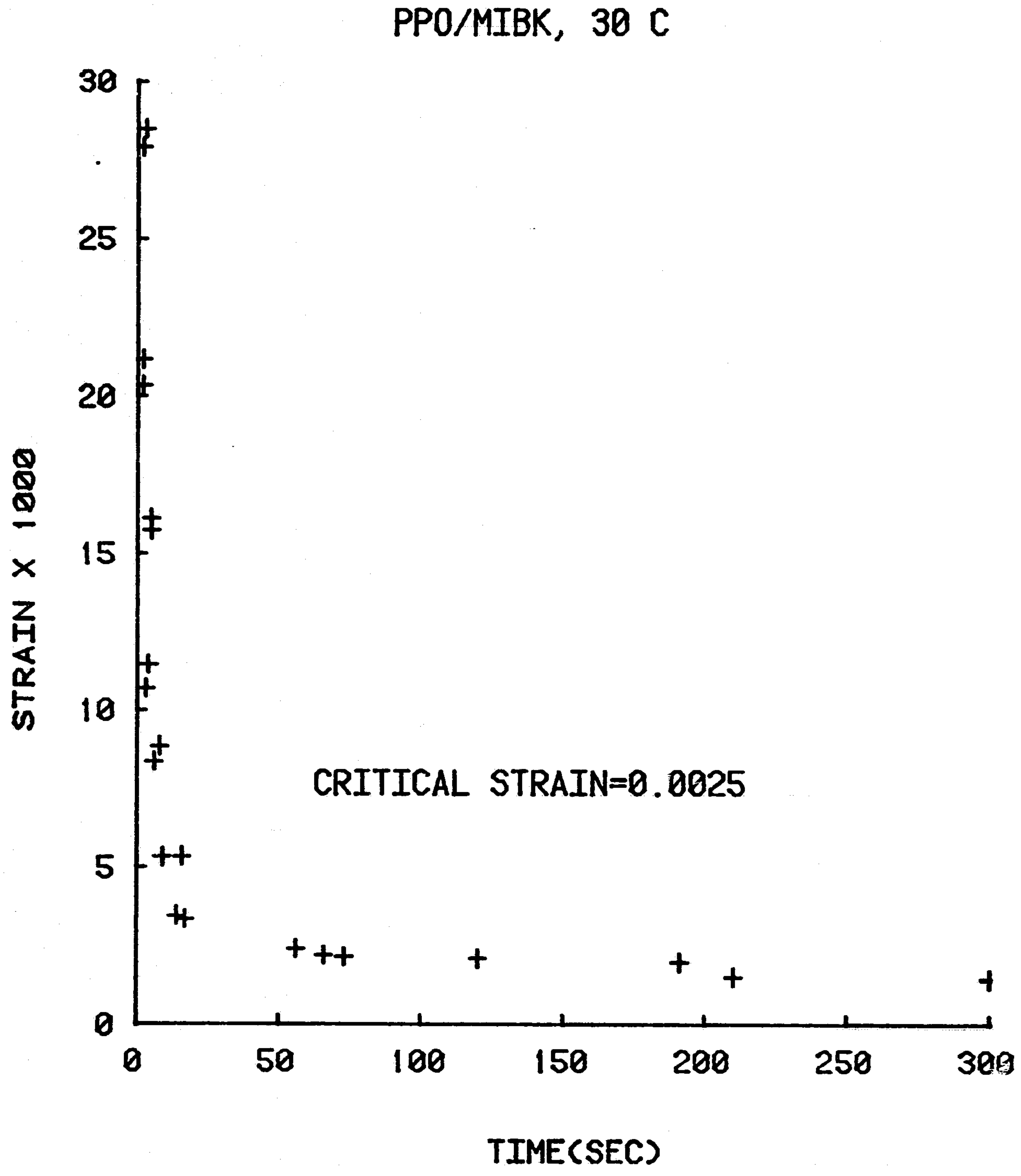
PP0/MIBK, 15 C


STRAIN X 1000
35
30
25
20
15
10
5
0
CRITICAL STRAIN=0.0032
0
50
100
150
200
250
300
TIME(SEC)

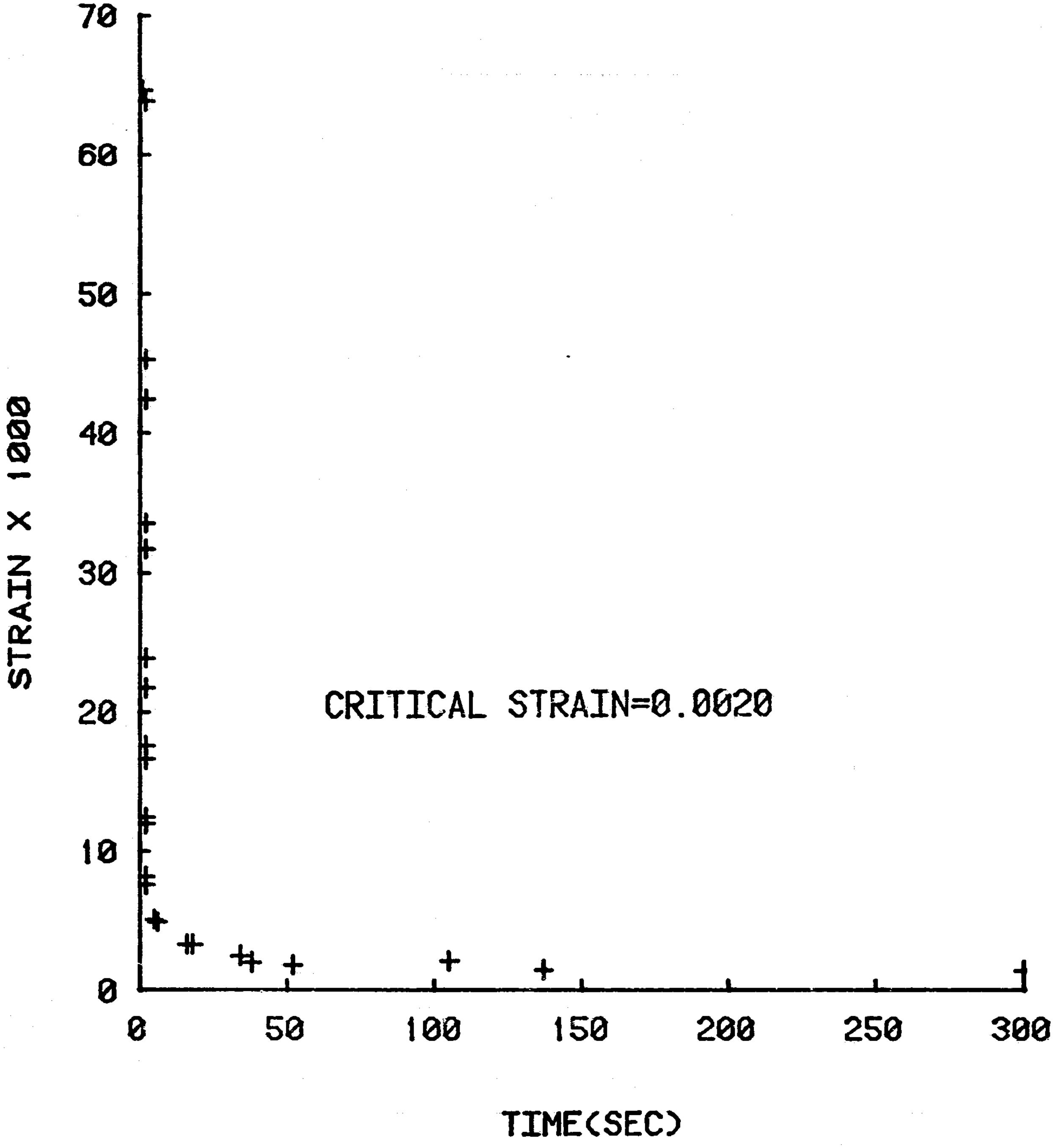

PPO/MIBK, 20 C
STRAIN X 1000
30
25
20
15
10
5
0
CRITICAL STRAIN=0.0025
0
50
100
150
200
250
300
TIME(SEC)

PPO/MIBK, 25 C


STRAIN X 1000
90
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
CRITICAL STRAIN=0.0019
TIME(SEC)

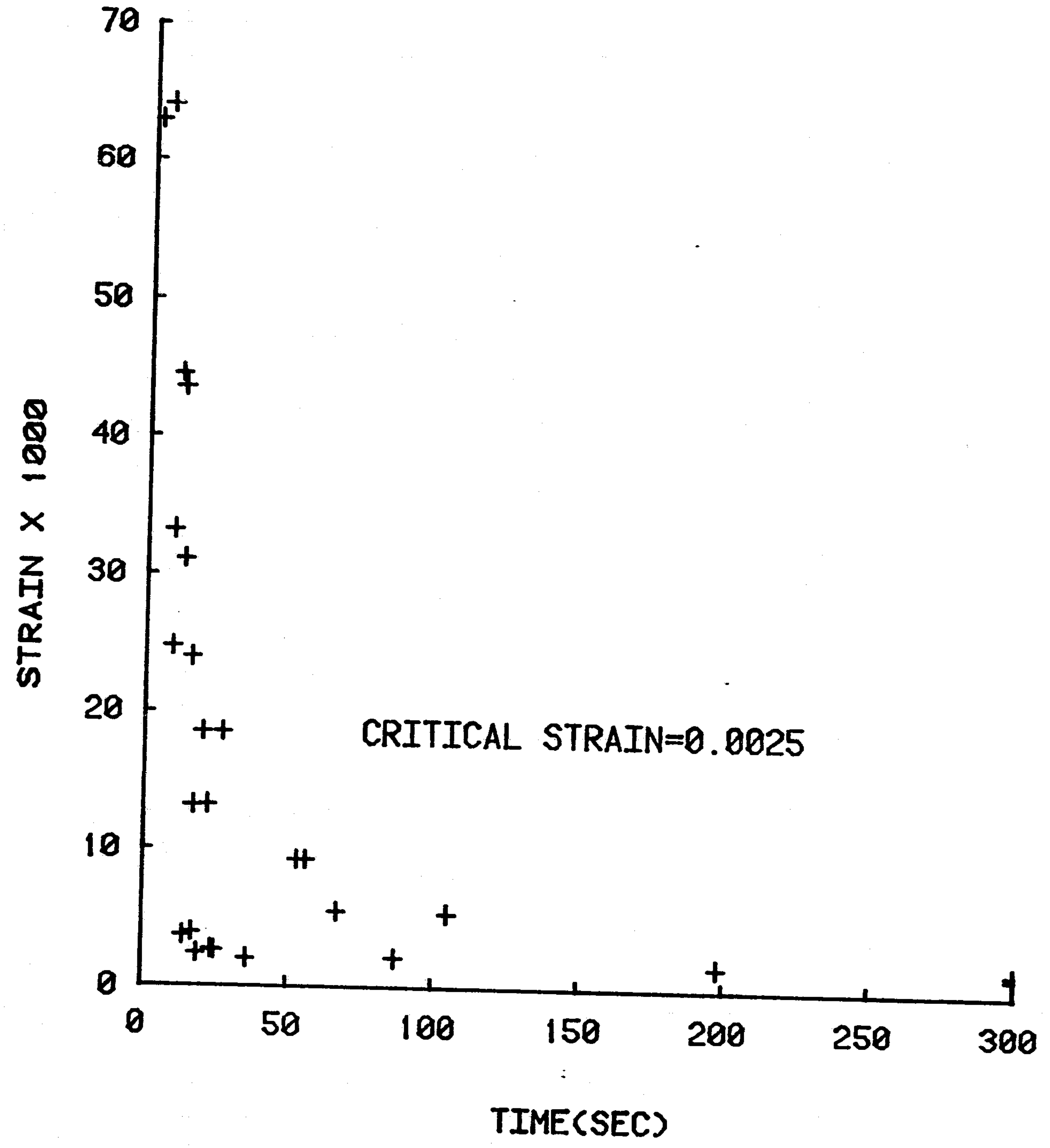

PPO/MIBK, 30 C
STRAIN X 1000
0
5
10
15
20
25
30
CRITICAL STRAIN=0.0025
0
50
100
150
200
250
300
TIME(SEC)

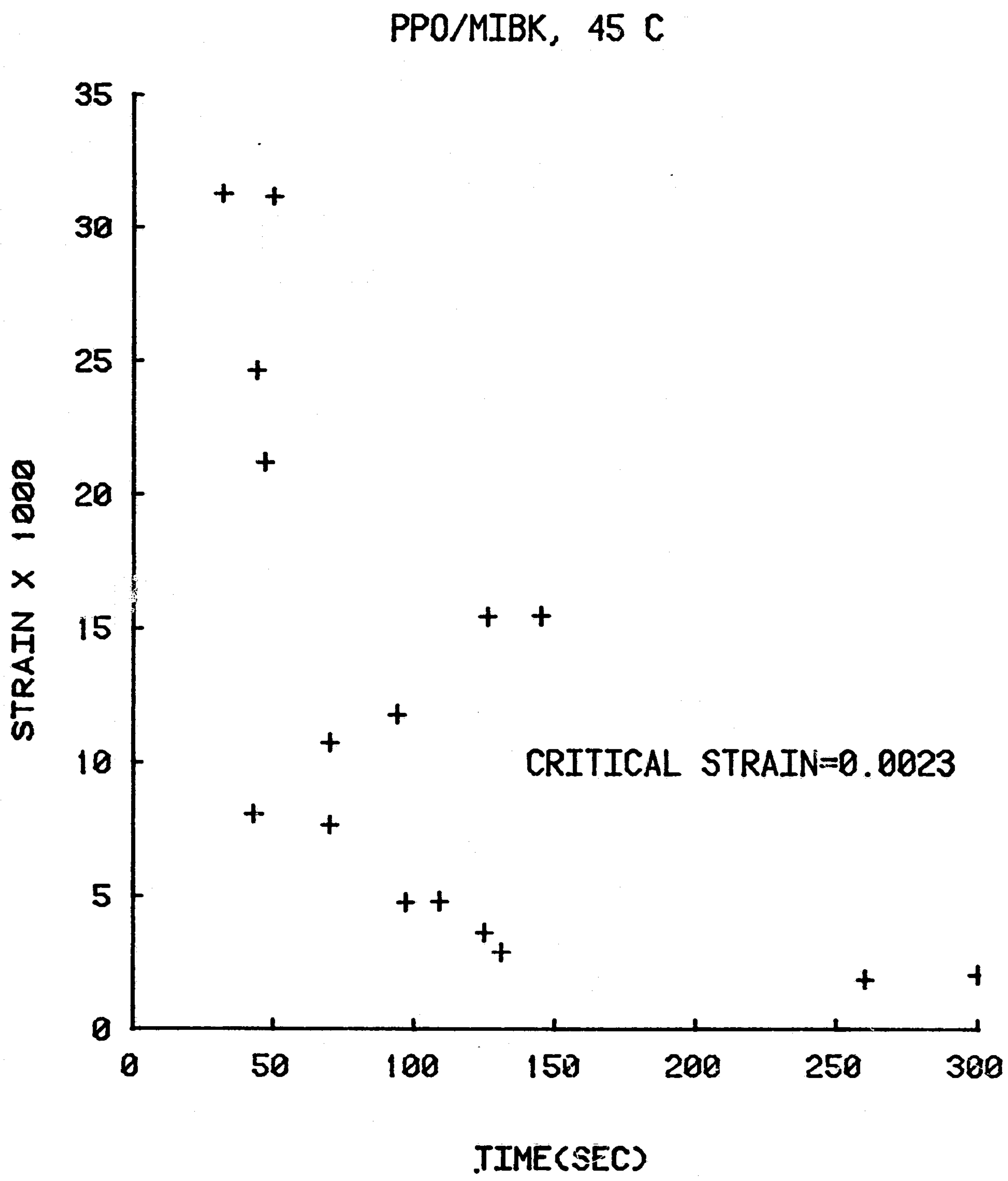
PPO/MIBK, 35 C



CRITICAL STRAIN=0.0020

PPO/MIBK, 40 C


STRAIN X 1000
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
TIME(SEC)
CRITICAL STRAIN=0.0025


PPO/MIBK, 45 C
STRAIN X 1000
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
TIME(SEC)
CRITICAL STRAIN=0.0023