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Secondary Crystallization in Polyethylenes

by

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Secondary Crystallization in Polyethylenes

The subject of this report concerns the changes that take place in phase structure of homopolymers and copolymers during long-time crystallization. Since the nature of the project requires long time periods, the order of several years or more, before completion and obtaining the final results, it is thought appropriate to submit a brief Summary Report. We do this at this time in particular since some very interesting results have already been obtained.

It is well known that the properties of crystalline polymers change over long time periods whether in storage or in use. These changes have generally been attributed to variation in the level of crystallinity and the concomitant influence on properties. With the deeper understanding of phase structure of crystalline polymers that has evolved in recent years it has become opportune to investigate this problem in more detail. Consequently we have studied changes in the phase structure of a set of polyethylenes which were rapidly crystallized from the melt (quenched to -78°C), stored at ambient temperature, and periodically sampled. Three unfractionated linear polymers were studied whose molecular weights were $M_w = 1.5 \times 10^5$, $M_n = 2 \times 10^6$ and $M_n = 8 \times 10^6$ respectively. In addition, a narrow molecular weight distribution hydrogenated polybutadiene, $M_w = 1.08 \times 10^5$, 2.2 mole percent ethyl branch points, was also studied. The hydrogenated polybutadiene is equivalent to a random polyethylene copolymer with ethyl branches.

Changes that took place in these polymers were studied by periodically measuring the density and the Raman internal modes. The Raman spectra yield the fraction of core crystallinity, α_c , the fraction of liquid-like region, α_l , and the fraction of the interfacial region, α_b . It has been found in the past that for a large number of polyethylene systems the core crystallinity α_c is the same as the level of crystallinity $(1-\lambda)_{\Delta H}$ that is determined from enthalpy of fusion measurements, i.e.

$$\alpha_c = (1-\lambda)_{\Delta H} \quad (1)$$

It is also known that the level of crystallinity determined from density, $(1-\lambda)_d$, is greater than α_c (and $(1-\lambda)_{\Delta H}$). However, based on a large amount of experimental data, $(1-\lambda)_d$ can be quantitatively expressed as

$$(1-\lambda)_d = \alpha_c + \alpha_b \quad (2)$$



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Thus the density determined level of crystallinity measures the core crystallinity as well as the contribution from the interfacial region.

These present studies have now been underway for a little more than 100 days with the following important findings. No changes have been observed, either in the density or Raman internal modes for the lowest molecular weight linear polyethylene sample, $M_w = 1.5 \times 10^5$. However, significant changes have been observed in the two higher molecular weight samples. Since the results were similar in both cases we illustrate the findings with the highest molecular weight sample. In Fig. 1 we plot the observed density as a function of log time. On a density basis the initial value corresponds to a level of crystallinity of 0.54 and increases to 0.57 after storage at ambient temperature for 100 days. The plot in Fig. 2 of the Raman internal modes reveals the accompanying changes in the phase structure. We find that the fraction of core crystallinity, α_c , remains constant over this time period. On the other hand the fraction of the liquid-like region, α_l , decreases from 0.48 to 0.41. This change is accompanied by a corresponding increase in the fraction of the interfacial region. Thus, we find the rather surprising result that the density increase does not in fact reflect an increase in the level of crystallinity. The core crystallinity remains constant. What is happening to the phase structure with time is that the partially ordered interfacial region further develops at the expense of the liquid-like region.

The results for the hydrogenated polybutadiene (a random ethyl branched copolymer) given in Figs. 3 and 4 are very similar. On a density basis the level of crystallinity increases from 0.35 to 0.39 over the 100 days of the present observation. This apparent change in the level of crystallinity is not reflected in the core crystallinity which remains constant at 0.23 (Fig. 4). However, the fraction liquid-like region decreases from 0.68 to 0.56 with a concomitant increase in the fraction of the interfacial region. Thus, the changes in the phase structure in the random copolymer and the high molecular weight homopolymers are very similar to one another.

The important conclusion that is reached to date from this work is that by storage of the polyethylenes at ambient temperature, a temperature that is well removed from the melting temperature and crystallization region, the core crystallinity does not change with time. However, the content of the partially ordered interfacial region increases at the expense of the completely disordered liquid-like region. These studies, and those continuing on, will set the basis for investigating and interpreting the changes in properties of crystalline polymers over long-time periods.

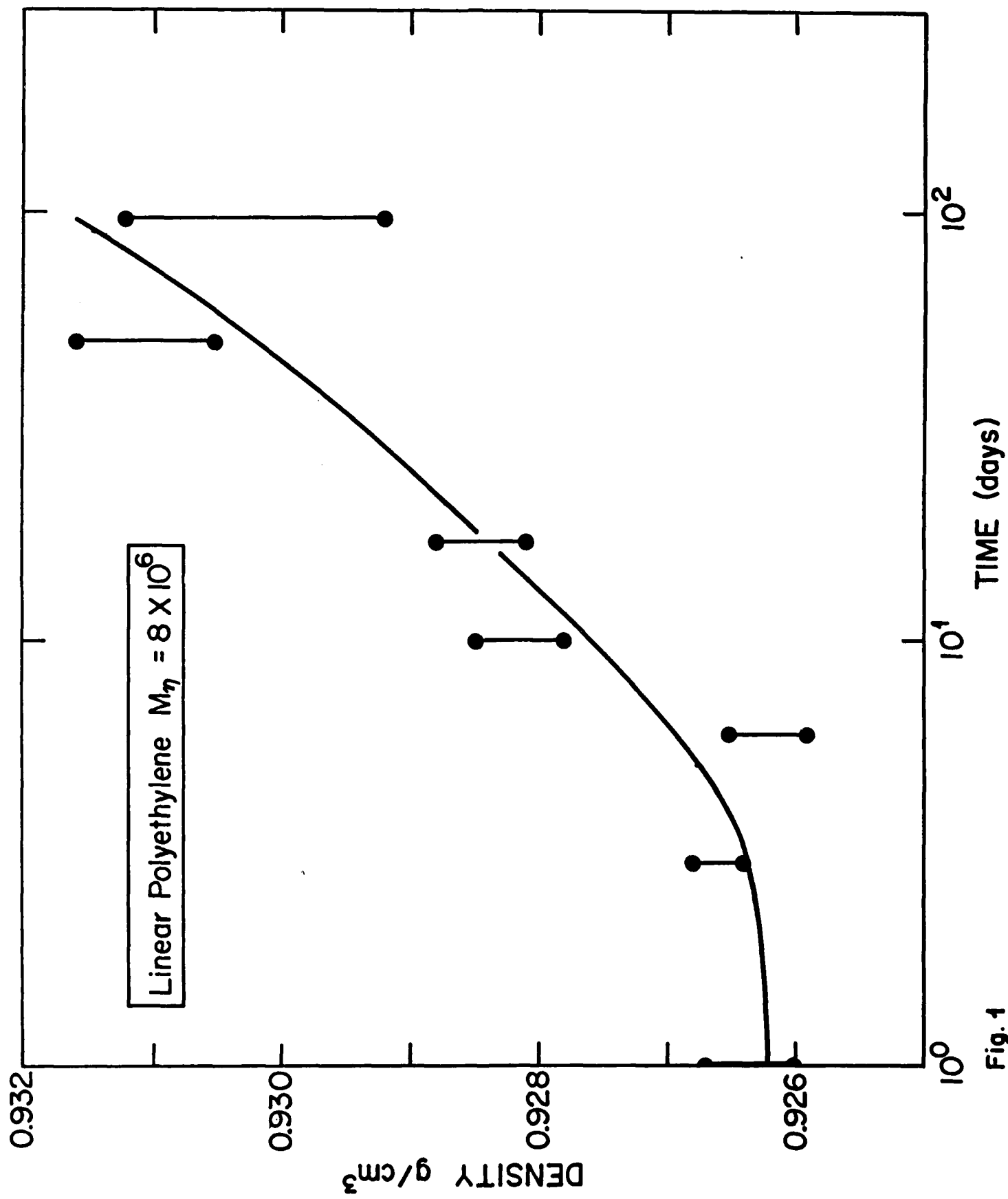


Fig. 1

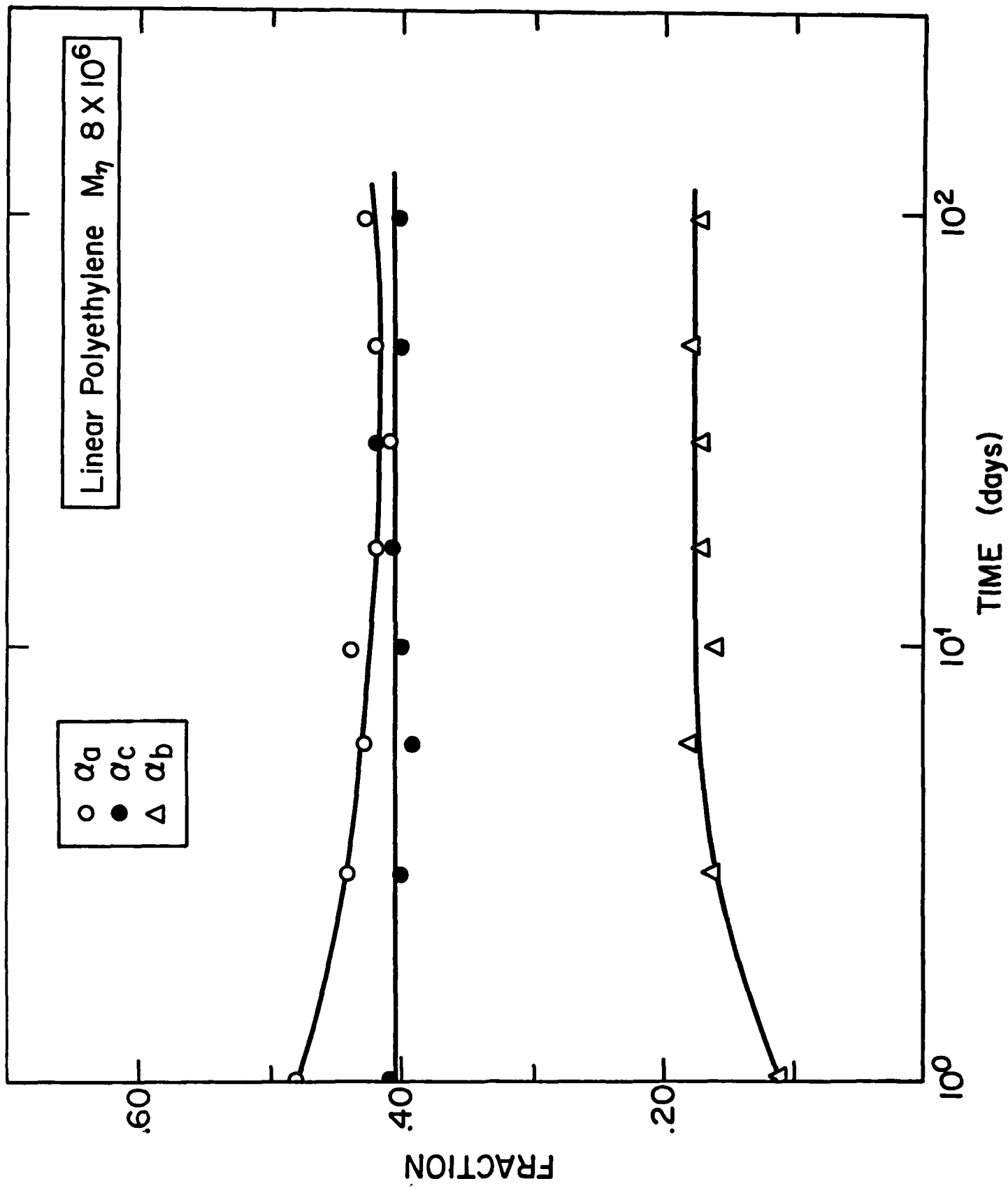


Fig. 2

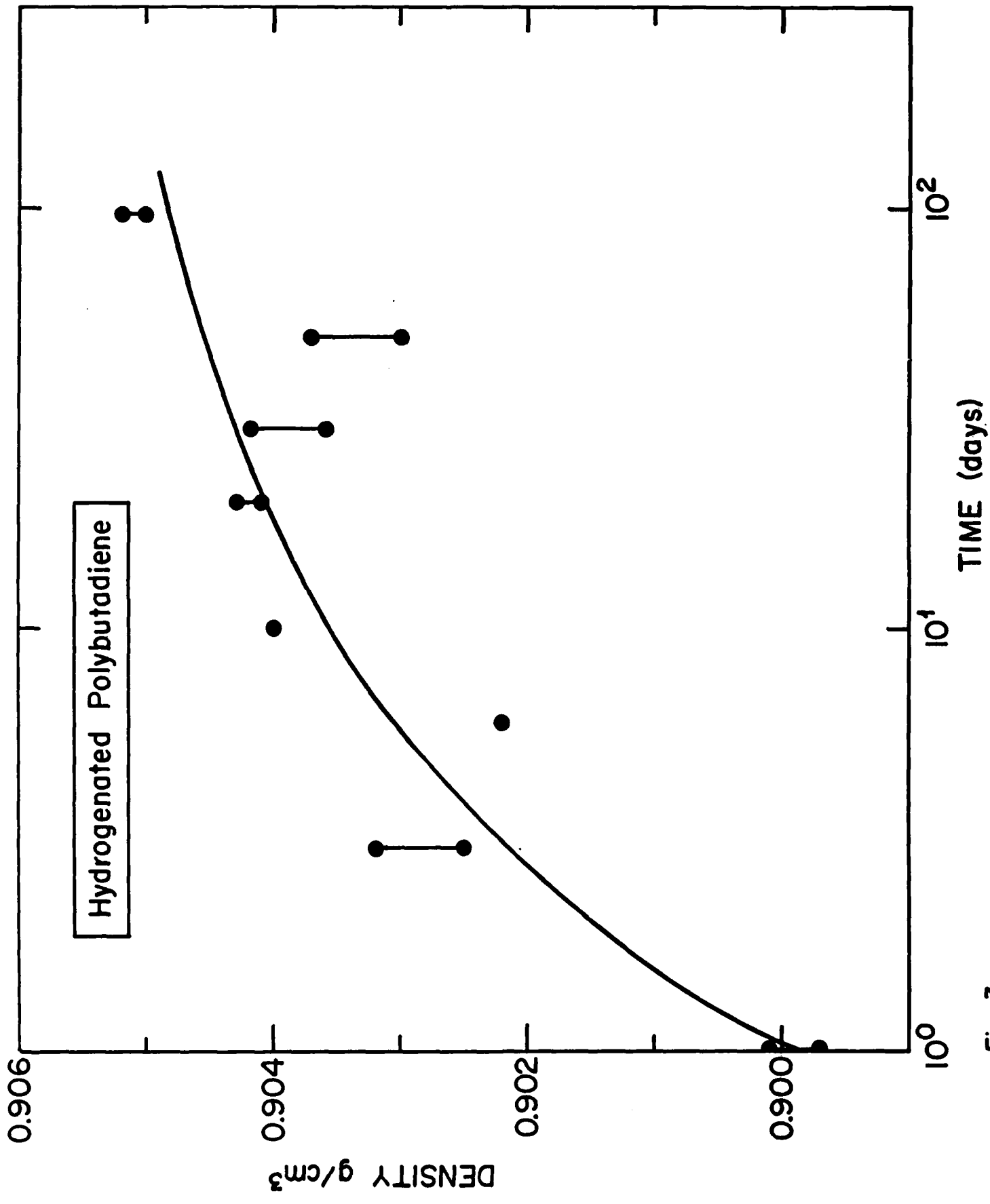


Fig. 3

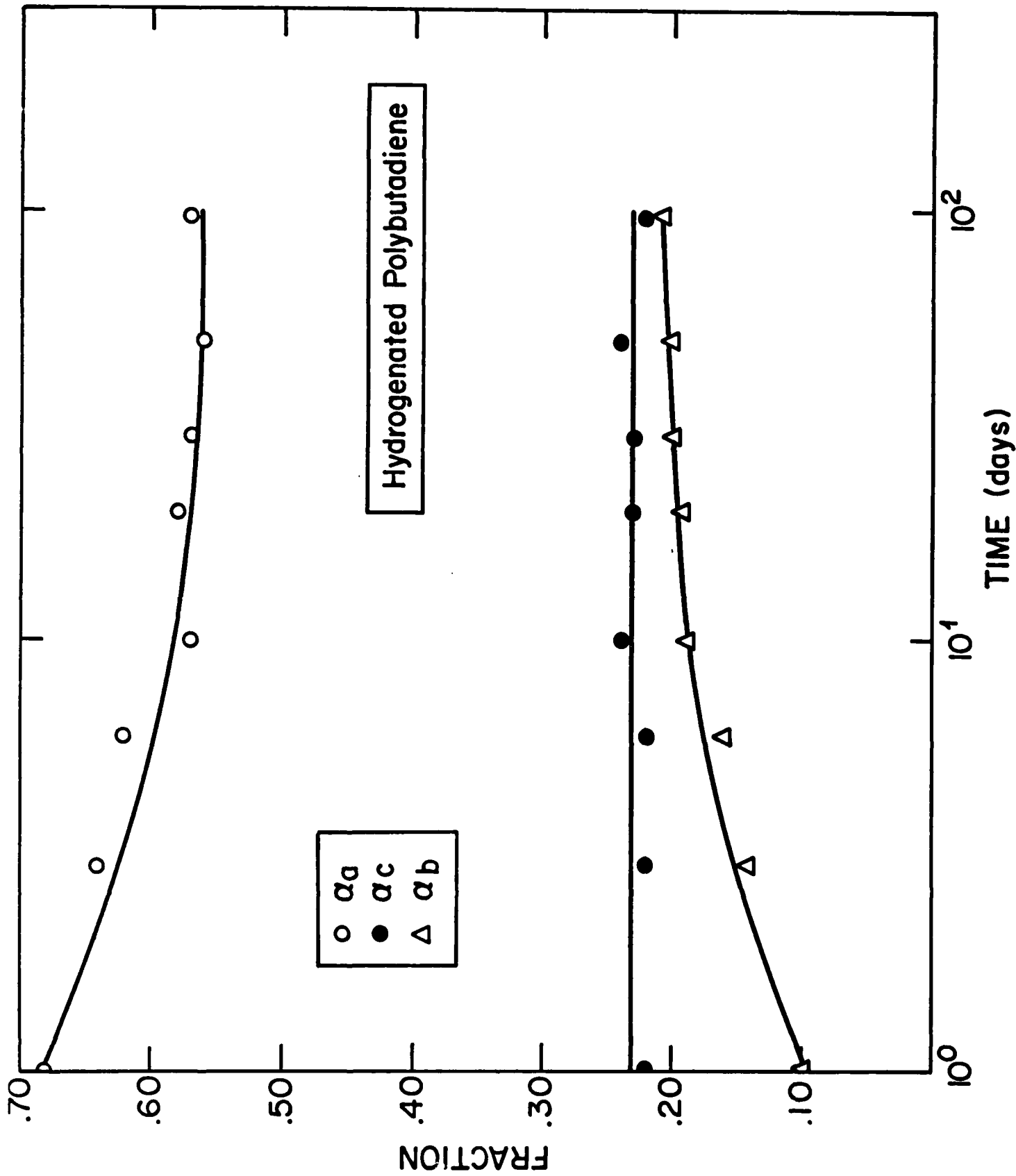


Fig. 4

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