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# MICROCELLULAR POLYMER FOAMS PREPARED BY THERMALLY-INDUCED PHASE SEPARATION

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**INTRODUCTION** Thermally-induced phase separation (TIPS) of polymer solutions is a versatile technique to prepare low-density polymer foams with properties that are necessary for some experimental high energy physics programs, such as inertial confinement fusion [1]. The process consists of three steps [2]. In the first step, a polymer and solvent are heated above their critical temperature to achieve a homogeneous polymer solution. Next, the solution is quenched in a controlled fashion in order to initiate thermally-induced phase separation, TIPS. Under some circumstances, TIPS can result in the formation of bi-continuous phases, a polymer-rich phase and a solvent-rich phase. Once phase separation has occurred, the solution can be frozen which effectively terminates phase separation. Alternatively with semi-crystalline polymers the solution may form a stable gel after TIPS. In the final step, the solvent is removed by sublimation of the frozen solvent or by liquid extraction of a resulting gel leaving behind a microcellular polymer foam. By controlling the phase separation during the quench, the foam morphology, foam density, and cell size can be varied.

**DISCUSSION** For noncrystallizable polymers, such as atactic polystyrene (PS), the cell size obtained from the TIPS process depends on many thermodynamic variables and the quench rate of the solution [2]. For a given quench rate, phase separation occurs in the solution from the time that the phase boundary is reached until the solvent is frozen (or the solution $T_g$ is reached). The length of time allowed for phase separation, then determines the final cell size since there is a thermodynamic driving force for complete phase separation. For fast quenches, the cell size can be submicron in size. For slower quenches, the cell size coarsens.

We have studied the coarsening process in demixed polystyrene solutions by quenching solutions at a given temperature in the two-phase region for times ranging from minutes up to one hour and observing how the cell size changes. The results are shown in Fig. 1 for four concentrations of PS/cyclohexane solutions. The slopes indicated on the log-log plot are consistent with coarsening occuring by a diffusive process rather than a hydrodynamic one [3]. A diffusive coarsening model developed specifically for demixed polymer solutions predicts the following relationship between the cell size, $d^{\beta}$ and coarsening time, t:

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$$(d^{\beta})^3 = \frac{32\ D_{ps}^{\beta}\ c_s^{\beta}\ c_p^{\beta}\,\sigma\,(V_p - V_s)\ [2(c_p^{\alpha} / c_p) - 1]^2}{9\ kT\ c_p^{\alpha}}\,t \quad (1)$$

where $D_{ps}$ is the diffusivity of the polymer in the solvent, V is the molar volume of either solvent (s) or polymer (p), $\sigma$ is the interfacial tension of the demixed phases, and c is the concentration of either solvent or polymer in the original homogeneous solution or else the dilute ($\beta$) or concentrated phase ($\alpha$) [3].

In the normal course of making a polystyrene foam, the solution is cooled from a single surface which results in a quench rate and a cell size gradient. This may be undesireable for some applications. To minimize coarsening one can utilize several stategies suggested by Eq (1). For semicrystalline polymers the polymer diffusivity can be reduced to zero by quenching below the crystallization temperature. This is the approach in phase separated gelation.

Gels are prepared by thermally quenching solutions of semi-crystalline polymers below the phase separation and crystallization temperatures. The gels are then extracted in a one or two step process. In the one step process liquid $CO_2$ is used to extract the gel and then removed super-critically. In the two step process the gel is first extracted with a nonsolvent for the polymer, (e.g. methanol or acetone), which is then extracted with super-critical $CO_2$. A typical $CO_2$ extractor is shown in Fig. 2. This process has been successfully applied to polyethylene, poly-4-methyl-1-pentene, polypropylene, polyacrylonitrile, and isotactic polystyrene. Because coarsening is eliminated with phase-separated gels, the process is quench rate insensitive. This results in foams of uniform cell size, small cell size, and in foams which are not limited in dimension. An example is the polyacrylonitrile foam shown in Fig. 3 which has a BET surface area of over 300 $m^2/g$ which corresponds to a cell size of 0.11 micrometers.

**CONCLUSIONS** The structure of phase separated polymer solutions will coarsen with time according to a diffusive mechanism. The coarsening law for polystyrene solutions is qualitatively given by Eq (1). Coarsening can result in a cell size gradient in foams made with the TIPS process and in a larger cell size than is theoretically possible. To minimize coarsening, one can use semi-crystalline polymers which can be made to crystallize after phase separation. The resulting foams have uniform and small cell sizes. Cell sizes as low as 0.1 micrometer have been obtained with both polyacrylonitrile and isotactic polystyrene foams made with this technique.

[1] A.T. Young, D.K. Moreno, and R.G. Marsters, J. Vac. Sci. Tech. 20, 1094 (1982).
[2] J.H. Aubert and R.L. Clough, Polymer, 26, 2047 (1985).
[3] J.H. Aubert, submitted to Macromolecules, (1989).

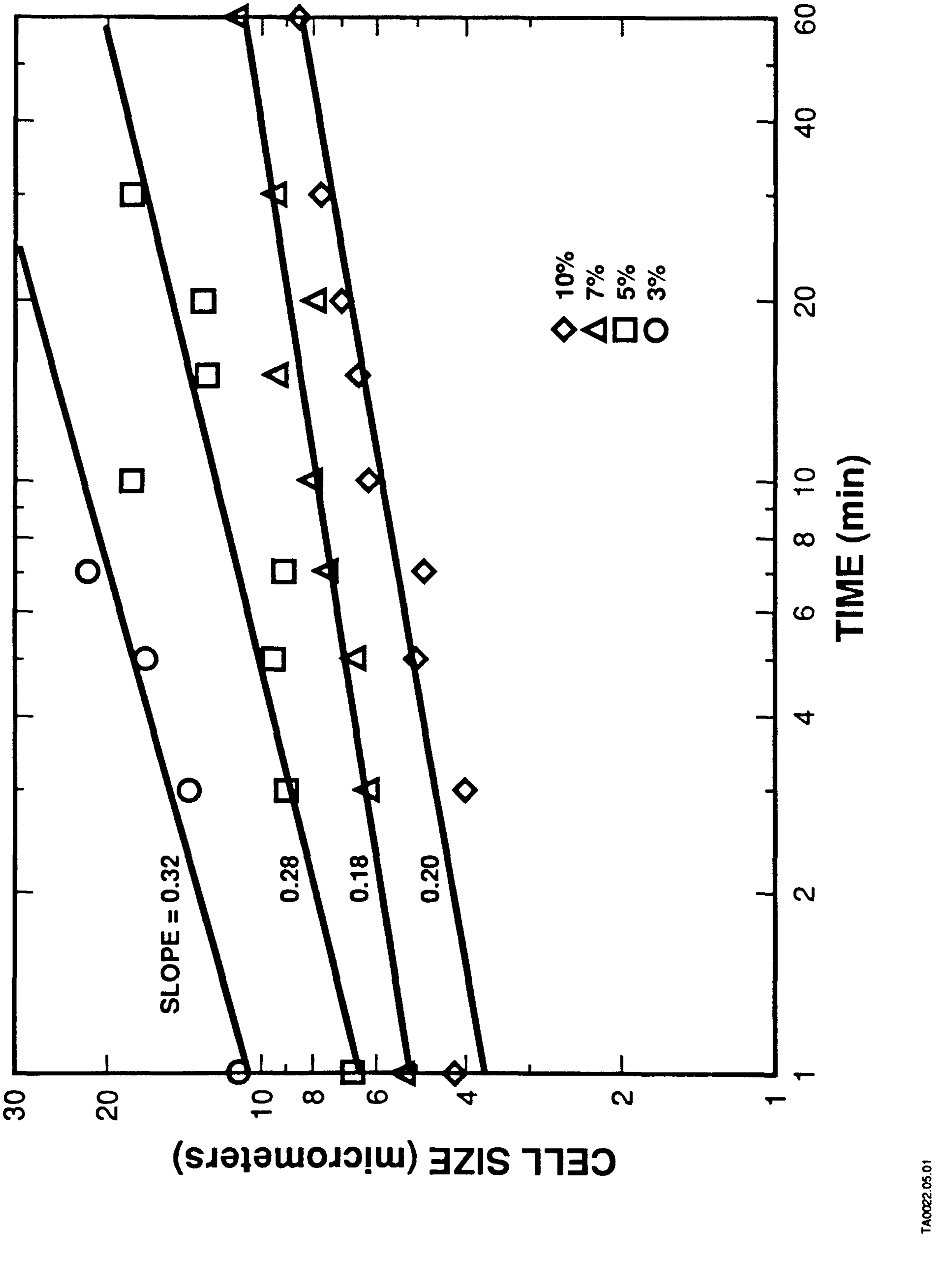

Fig. 1. Results for coarsening studies on demixed polystyrene/cyclohexane solutions from ref. [3]. Polystyrene $M_w = 2.23 \times 10^6$, quench temperature 27 C.

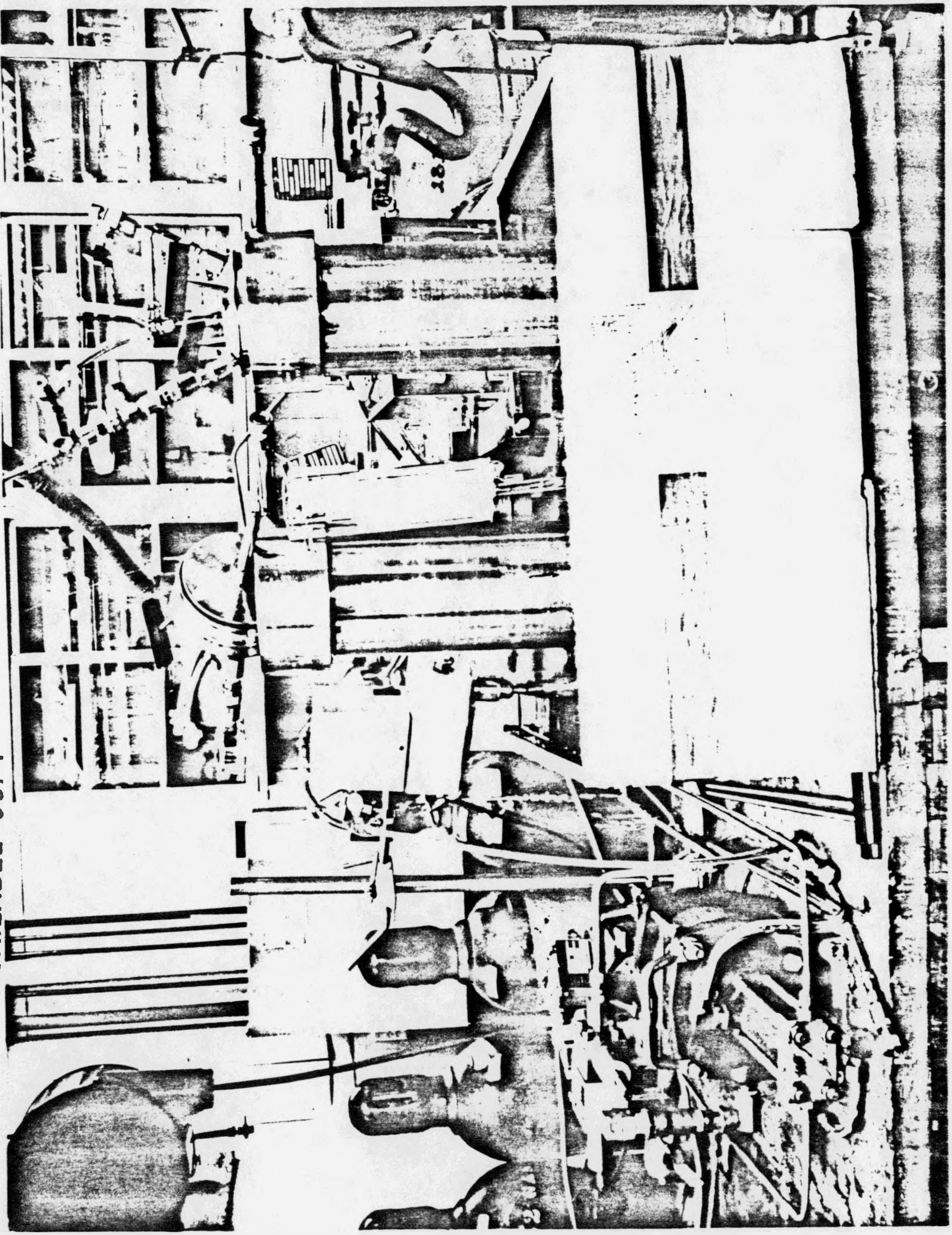

Fig. 2. Carbon dioxide extraction system. Overflow or siphon cups are used for both sub-critical and super-critical extractions.

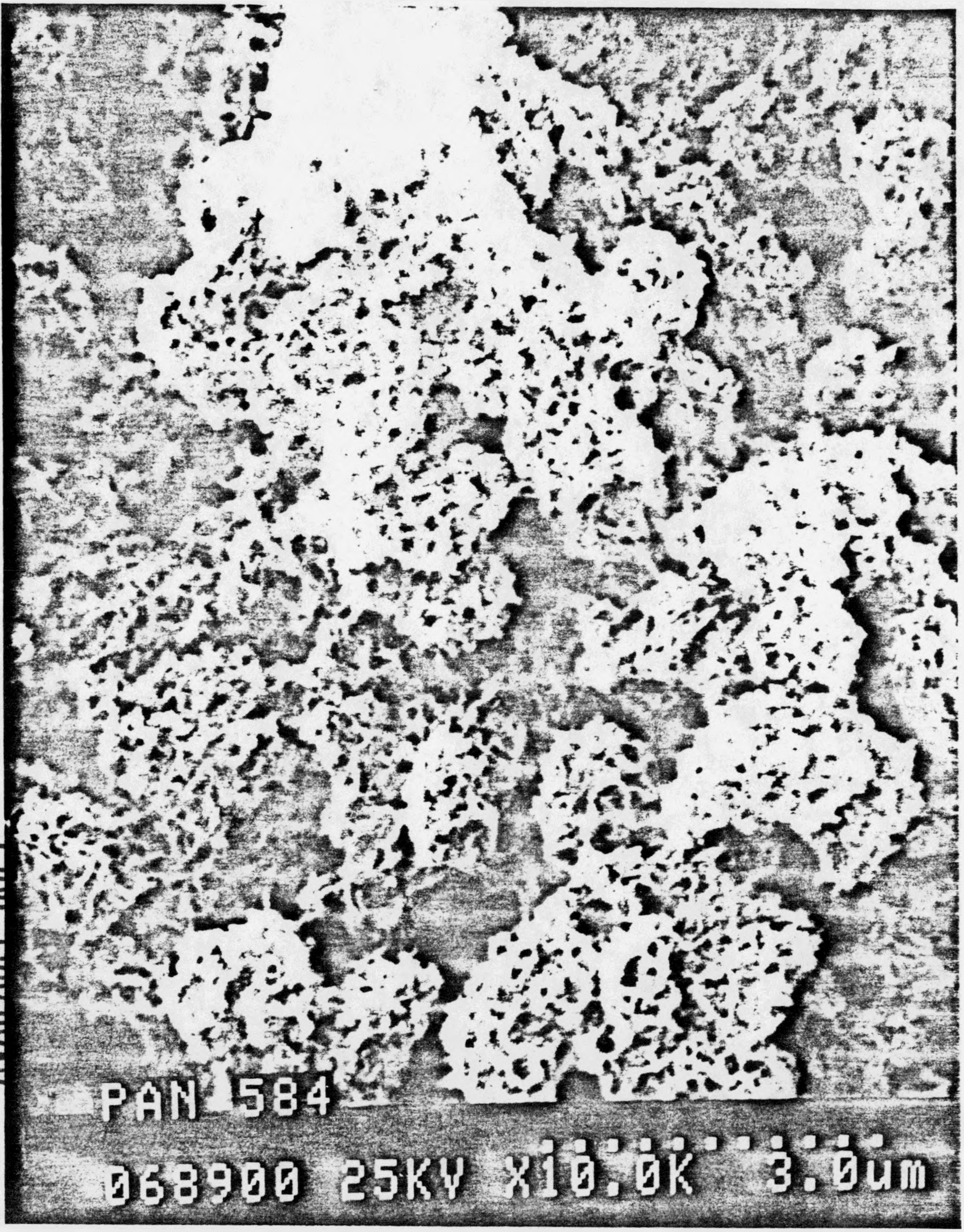

Fig. 3. Polyacrylonitrile foam of density 0.12 g/cm$^3$ and BET surface area 305 m$^2$/g. The bar marker is 3.0 micrometers.