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Molecular Configuration in Bulk Polymers†

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Experimental results on the following topics are examined and discussed from the point of view of their bearing on the molecular configurations and intermolecular correlations in amorphous polymers: (i) the effect of dilution on the force of retraction f in stretched elastomers; (ii) the effect of dilution on the force-temperature coefficient, and the correspondence of $-\left[\partial \ln(f/T)/\partial T\right]_{V,L}$ to $d \ln \langle r^2 \rangle_0/dT$ found for the linear polymer in dilute solution; (iii) comparison of experimental cyclization constants K_x for siloxanes, both in absence and in presence of an inert diluent, with values calculated from dimensions ($\langle r^2 \rangle_0$) for the linear polymer; (iv) thermodynamic activities of solutions in the Henry's law range; (v) meager results currently available from direct determination of dimensions of polymer chains in the bulk polymer; (vi) depolarized light scattering and the effect thereon of dilution with an isotropic diluent; and (vii) strain birefringence and the effects of dilution on the stress-optical coefficient. Optical anisotropies from (vi) and (vii) and their dependence on concentration indicate local intermolecular correlations, which, however, appear to be not much greater than for simple liquids. None of the experiments (i) to (iv) gives any intimation of an effect of dilution that could be ascribed to dispersal of an ordered arrangement of chains. Results from (ii) and (iii) demonstrate that the same chain configurational parameters found in dilute solutions hold quantitatively in the bulk polymer. Evidence is thus compelling that chain configurations in the bulk amorphous polymer differ inappreciably from the configurations in a dilute solution, apart from effects of excluded volume in the latter environment.

†Lecture at the Scientific Symposium at the occasion of the Dedication of Midland Macromolecular Institute, September 29, 1972. The paper will be published in full in *Pure and Applied Chemistry*.