(10) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1981**, *14*, 224.
(11) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Polym. Bull.* **1981**, *4*, 241.
(12) Broze, G.; Jérôme, R.; Teyssié, Ph.; Gallot, B. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 415.
(13) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 920.
(14) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 1300.
(15) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2205.
(16) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Macromolecules* **1983**, *16*, 1771.

Density Profiles of Polymer-Containing Nuclei

YITZHAK RABIN† and HOWARD REISS*

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024.

Received March 26, 1984

In a recently reported experiment, gas-phase polymerization was successfully demonstrated in supersaturated monomer vapor.[1] Due to the sharp threshold behavior of the nucleation process, once the polymer grows to a certain critical size it serves as a nucleus for inhomogeneous nucleation of vapor monomers, and the resulting polymer-containing droplet condenses out of the vapor. The critical droplet was analyzed in the framework of a surface-modified, Flory–Huggins-type model,[2] which gave the polymer size dependence of the nucleation barrier and the effective surface tension of the droplet[3].

In this note we present a model for density profiles of polymer-containing droplets, accounting for polymer chain connectivity and finite droplet size effects. The model combines a modified version of the lattice-fluid (LF) theory[4] with the self-consistent field (SCF) theory of polymer chains in solvents.[5–7]

The model is of some general interest, since the problem does not seem to have been addressed previously, although studies of the interface between a bulk polymer solution and its vapor have been performed. The present problem is not only of interest to the theory of nucleation but also to the field of air pollution, where very small particles of polymer solution may be in quasi-equilibrium with ambient vapors (although in this case we are concerned with "stable" rather than "unstable" equilibrium).

Neglecting the polymer entropy of mixing term (a single polymer inside a droplet) and assuming equilibrium between monomers in the droplet and in the surrounding vapor, the square-gradient approximation to the chemical potential gives[4–7]

$$-\left(\frac{\partial^2}{\partial r^2}+\frac{2\partial}{r\partial r}\right)\rho(r) - 2(\rho(r)-\rho(\infty)) + T\left(\frac{1}{l_{\mathrm{m}}}\ln\frac{\rho_{\mathrm{m}}(r)}{\rho(\infty)} - \ln\frac{1-\rho(r)}{1-\rho(\infty)}\right) = 0 \qquad (1)$$

where we assume that the monomer and polymers differ only in their length parameters (l_{m} and $l_{\mathrm{p}} \gg l_{\mathrm{m}}$, respectively[8]) and that the droplet is spherically symmetric. Also, $\rho(r) = \rho_{\mathrm{m}}(r) + \rho_{\mathrm{p}}(r)$, $\rho_{\mathrm{m}}(r)$ ($\rho_{\mathrm{p}}(r)$) being the local monomer (polymer) density. The distance r and temperature T are scaled in appropriate units.[8]

Using the SCF theory of polymer chains, in the long-chain limit[6] we obtain $\rho_{\mathrm{p}}(r) = (N_{\mathrm{p}}/4\pi)(\psi^2(r)/r^2)$, where N_{p} is the number of statistically independent polymer chain segments (each of length b_{p}) and $\psi(r)$ is the normalized eigenfunction corresponding to the lowest eigenvalue (E_0) of the Schrödinger-like equation

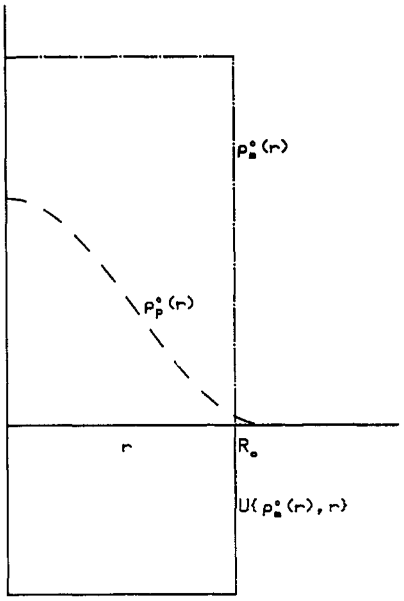


Figure 1. Solvent density profile $\rho_{\mathrm{m}}^{(0)}(r)$ (– · –) and the corresponding SCF potential $U[\rho_{\mathrm{m}}^{(0)}(r),r]$ (—). The resulting polymer density profile $\rho_{\mathrm{p}}^{(0)}(r)$ is given by the dashed line.

$$\left(-\frac{b_{\mathrm{p}}^2}{6}\frac{\partial^2}{\partial r^2} + U[\rho_{\mathrm{m}}(r),\rho_{\mathrm{p}}(r)]\right)\psi(r) = E_0\psi(r) \qquad (2)$$

subject to the boundary conditions

$$\frac{\partial}{\partial r}\left(\frac{\psi}{r}\right)^2\Bigg|_{r=0} = 0; \qquad \psi(\infty) = 0$$

The SCF potential $U[\rho_{\mathrm{m}},\rho_{\mathrm{r}}]$ is given by

$$U[\rho_{\mathrm{m}}(r),\rho_{\mathrm{p}}(r)] = -\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\rho(r) - 2(\rho(r)-\rho(\infty)) - T\ln\frac{1-\rho(r)}{1-\rho(\infty)} \qquad (3)$$

For a given temperature (T) and monomer pressure (determining $\rho(\infty)$), eq 1–3 can be solved numerically, resulting in the density profile $\rho_{\mathrm{p}}(r)$, $\rho_{\mathrm{m}}(r)$.[9] Here, we present a semianalytical solution for the case of a large, polymer-dilute droplet (small polymer volume fraction). We try an iterative solution, first using eq 1 with $\rho_{\mathrm{p}}(r) = 0$ to obtain the density profile $\rho_{\mathrm{m}}^{(0)}(r)$ of a homogeneous critical nucleus with radius R_0, and then compute the SCF potential $U[\rho_{\mathrm{m}}^{(0)}(r),0]$ and use it to solve eq 2 for the polymer density profile $\rho_{\mathrm{p}}^{(0)}(r)$. The latter is then used in eq 1 to compute a corrected value for the monomer density profile ($\rho_{\mathrm{m}}^{(1)}(r)$) and the iteration continues until convergence is obtained.

Taking $\rho_{\mathrm{m}}^{(0)}(r) = \rho_{\mathrm{m}}^{(0)}(0)\theta(R_0 - r)$, where θ is the theta function, the SCF potential has a "square well" form (Figure 1). Application of the variation method[10] gives

$$\rho_{\mathrm{p}}^{(0)}(r) = \frac{2\pi^2}{3}\left(1 - \frac{3\delta}{\pi}\right)\frac{N_{\mathrm{p}}}{(4\pi/3)R_0^3}\,\frac{\sin^2[\pi(1-\delta/\pi)(r/R_0)]}{[\pi(1-\delta/\pi)(r/R_0)]^2}, \qquad r \le R_0 \qquad (4a)$$

$$\rho_{\mathrm{p}}^{(0)}(r) = \frac{2}{3}\delta^2\frac{N_{\mathrm{p}}}{(4\pi/3)R_0^3}\,\frac{e^{-2\pi\delta(r-R_0)/R_0}}{(r/R_0)^2}, \qquad r \ge R_0 \qquad (4b)$$

---

† Present address: Center for Studies of Nonlinear Dynamics, La Jolla Institute, La Jolla, CA 92037.

0024-9297/84/2217-2450$01.50/0

where we include lowest order corrections in $\delta = (\pi/3)(b_p/R_0)[l_m/(2|\ln \rho(\infty))|]^{1/2}$. Estimating the experimentally controlled parameters, $T \simeq 0.5$, $l_m \simeq 10$, $\rho_m(0)/\rho_m(\infty) \simeq 300$, we find that the solutions converge rapidly (i.e., are close to $\rho_p(0)$ and $\rho_m(0)$) provided that the polymer volume fraction in the nucleus, $N_p/(4\pi/3)R_0^3\rho_p^*$, is much smaller than 0.15 (ρ_p^* is the close-packed polymer density). Corrections lead to a slight increase of size of the critical droplet due to chain penetration into the droplet–vapor interface driven by entropy of confinement effects[6] (of order $(b_p/R_0)^2$).

We conclude this note by commenting on an interesting aspect of polymer growth in supersaturated vapor. In the absence of nucelation, low temperature and polymer concentration will lead to a collapsed (globular) state of the polymer chain.[6] However, once enough monomers are adsorbed on the polymer, the critical droplet size is reached and the droplet proceeds to grow to macroscopic dimensions. The polymer chain expands inside the droplet until the swollen configuration corresponding to a polymer in good solvent is reached. Thus, the nucleation process is accompanied by the globule-to-coil transition of the polymer.

Acknowledgment. Although the information in this document has been funded by the U.S. Environmental Protection Agency under assistance agreement CR 807864-02-0 to the National Center for Intermedia Transport Research, it does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

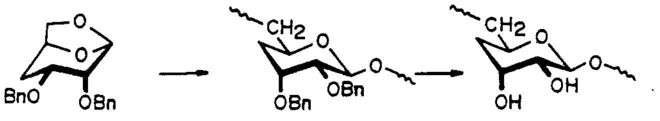
References and Notes

(1) M. A. Chowdhury, H. Reiss, D. R. Squire, and V. Stannett, *Macromolecules*, **17**, 1436 (1984).
(2) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953.
(3) H. Reiss and M. A. Chowdhury, *J. Phys. Chem.*, **87**, 4599 (1983).
(4) I. C. Sanchez, *J. Macromol. Sci., Phys.*, **B17**, 565 (1980).
(5) E. Helfand and A. M. Sapse, *J. Polym. Sci., Polym. Symp.*, **No. 54**, 289 (1976).
(6) I. M. Lifshitz, A. Y. Grosberg, and A. R. Khokhlov, *Rev. Mod. Phys.*, **50**, 683 (1978).
(7) K. M. Hong and J. Noolandi, *Macromolecules*, **14**, 1223 (1981).
(8) I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, **80**, 2352 (1976).
(9) Y. Rabin and M. A. Chowdhury, to be published.
(10) L. I. Schiff, "Quantum Mechanics", 3rd ed., McGraw-Hill, New York, 1955.

Communications to the Editor

Chemical Synthesis of Polysaccharides. 4. 4-Deoxy-(1→6)-β-DL-*ribo*-hexopyranan, the First Example of a (1→6)-β-Linked Polysaccharide Synthesized by the Ring-Opening Polymerization Method

In recent years, a variety of polysaccharides and their analogues have been synthesized by the cationic ring-opening polymerization of anhydrosugar derivatives.[1-6] Above all, the polymerization of 1,6-anhydrosugar derivatives has been most extensively investigated, since it often yields high molecular weight stereoregular polymers exclusively composed of (1→6)-α-pyranosyl residues under appropriate reaction conditions, particularly at low temperatures. With the rise in polymerization temperature, the stereoregularity of the polymers is generally lost because of the concomitant formation of (1→6)-β-pyranosyl residues along with the predominant (1→6)-α-pyranosyl residues.[7] To the best of our knowledge, there has been no publication dealing with the chemical synthesis of polysaccharides predominantly or exclusively consisting of (1→6)-β-pyranosyl residues from 1,6-anhydrosugar derivatives. In the present communication, we report the chemical synthesis of 4-deoxy-(1→6)-β-DL-*ribo*-hexopyranan (**3**) by the ring-opening polymerization of a bicyclic acetal (**1**) derived from noncarbohyrates sources, followed by debenzylation of the resulting polymer (**2**).[8] This is the first example of a regularly (1→6)-β-linked polysaccharide obtained by the ring-opening polymerization method.



1 Bn, $-CH_2C_6H_5$ 2 3

Monomer **1**, 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (1,6-anhydro-2,3-di-*O*-benzyl-4-deoxy-β-DL-*ribo*-hexopyranose), was synthesized from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) via five reaction steps: The precursor of **1**, 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane, was prepared by the procedures described by Brown et al.[9-11] with some modifications. Subsequent benzylation of the dihydroxy compound by the conventional method using sodium hydride and benzyl chloride in dimethyl sulfoxide gave monomer **1** as white crystals. The monomer was purified by recrystallization three times from ethanol and finally from a mixture of *n*-hexane and dichloromethane (2.5:1 volume ratio): mp 42.5–43.5 °C; ^{13}C NMR ($CDCl_3$, 50 MHz, Me_4Si) δ 138.34 and 138.17 (phenyl (ipso)), 128.18 (phenyl (meta)), 127.73 (phenyl (para)), 127.39 and 127.19 (phenyl (ortho)), 100.51 (C(5)), 73.74 (C(3)), 72.91 (benzyl), 71.94 (C(4)), 71.10 (C(1)), 70.31 (benzyl), 66.81 (C(7)), 32.47 (C(2)) (the numbering is based on the IUPAC nomenclature of organic chemistry). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.71; H, 6.80.

Polymerization of **1** was carried out in three different solvents, toluene, dichloromethane, and 1-nitropropane, with phosphorus pentafluoride as initiator at −60 °C. A high-vacuum technique was employed for the polymerization. A polymer was separated from the reaction mixture by repeated reprecipitation using dichloromethane and methanol as a solvent–precipitant pair, followed by freeze-drying from a benzene solution. The results of the polymerization are presented in Table I.

The polymer prepared in toluene showed a higher melting point (Table I) and lower solubility than the polymers obtained in the other two solvents: The former polymer was soluble in benzene, chloroform, dichloromethane, 1,2-dimethoxyethane, and pyridine and insoluble in 1,4-dioxane, dimethylformamide, 1-nitropropane, and toluene, whereas the latter polymers were soluble in all these solvents. Such remarkable differences conceivably

0024-9297/84/2217-2451$01.50/0