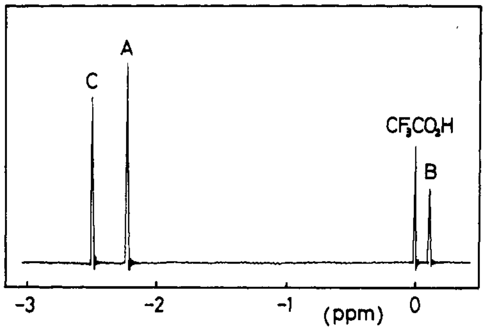

Figure 2. ^{19}F NMR spectrum of the oxepane polymerization system in nitrobenzene at 35° after 23 min; $[M]_0 = 2.80$ mol/l., $[I]_0 = 0.55$ mol/l. Chemical shifts are given in ppm relative to an external standard of CF_3CO_2H capillary.

In CCl_4 with $EtOSO_2CF_3$ initiator, a proton signal due to **2a** was not distinctly observed probably owing to the limitation of resolution and sensitivity of ^1H NMR. However, ^{19}F NMR clearly showed the presence of **2a** in about 10% for **3a.** Rate constants obtained were $k_i = 0.68 \times 10^{-5}$ l./(mol sec) and $k_{p(ap)} = 0.33 \times 10^{-5}$ l./(mol sec) in CCl_4 at 35°, respectively.

With the use of $MeOSO_2F$ initiator in nitrobenzene, ^{19}F signals of $MeOSO_2F$, the oxonium counteranion **2b,** and the macroester **3b** appeared respectively at −109.3, −116.8, and −112.7 ppm as sharp singlets. The $[O^+]$ fraction was very small, e.g., about 4% after equilibration.

In CCl_4 with fluorosulfonate initiator, on the other hand, only macroester **3b** could be seen by ^{19}F NMR spectroscopy, and the ion **2b** was not detected at all by ^{19}F NMR spectroscopy. With $EtOSO_2F$ initiator in the oxepane polymerization $k_i = 0.34 \times 10^{-5}$ l./(mol sec) and $k_{p(ap)} = 0.15 \times 10^{-5}$ l./(mol sec) were obtained. Furthermore, the propagating species of fluorosulfonate system was exclusively **3b** even in CH_2Cl_2, a more polar solvent than CCl_4. In cases where the concentration of **2b** could be taken as null, $k_{p(ap)}$ may be taken to be equal to $k_{p(e)}$ as observed in the tetrahydrofuran polymerization initiated by $EtOSO_2F$ in CCl_4.[1] However, the possibility of the contribution of ionic propagating species which might be present in a very small amount cannot be ruled out at the present stage of kinetic analysis.

Thus, it has been shown that rate constants (both k_i and $k_{p(ap)}$) and the $[O^+]$ fraction of the propagating end were very dependent upon the solvent employed. The equilibrium concentration of $[O^+]$ of the oxepane polymerization was always much lower than that of the tetrahydrofuran polymerization in the same solvent.[1,2]

This type of ion $\rightleftarrows$ ester equilibria including the polymerization system of tetrahydrofuran may be related to other types of reactions. In the solvolysis of ω-methoxy-*n*-alkyl *p*-bromobenzenesulfonates Winstein et al. observed a considerable rate enhancement for the butyl and pentyl derivatives,[13] which is interpreted in terms of neighboring-group participation involving cyclic trialkyloxonium intermediates.[13-15]

More detailed studies on the kinetics and mechanism will be published later.

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Partial Molar Volume of a Polymer in Supercritical Solution

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In supercritical solution deviations of the partial molar volume from the molar volume can give rise to thermodynamic anomalies and, according to transition state theory, to kinetic ones as well. Negative partial molar volumes of the less volatile component can occur, for example, in supercritical ethane–*n*-heptane mixtures and are attributable to the size difference between the two components of a homologous series.[1] The question as to whether such effects are sufficiently large in supercritical polymer solutions to be of thermodynamic or kinetic significance is of interest and important, for example, in connection with the free-radical polymerization of ethylene[2] which is carried out in supercritical solution.[3] An experimental determination of the partial molar volume of the polymer is difficult under such conditions.

The equation of state of Flory, Orwoll, and Vrij[4] (FOV) allows one to make reasonable estimates of molar and, within certain limits, of partial molar volumes for supercritical ethane–*n*-heptane mixtures.[1] We wish to show how a reduced equation of state, such as that of FOV, can be used to calculate the partial molar volume of a polymer in supercritical solution to obtain results which are good enough to settle questions such as that raised.

We consider a homologous binary mixture of solvent and polymer (ethane–polymethylene is a sufficiently good model for ethylene–polyethylene) and characterize it by the reduced variables $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$, $\tilde{P} = P/P^*$, where the quantities with asterisks and without superscripts refer to the reference parameters and molar properties of the mixture, respectively. The mixture parameters (unsubscripted) are related to those of the components (subscripted) by $V^* = x_1V_1^* + x_2V_2^* = v^*(r_1x_1 + r_2x_2)$, $\tilde{T} = \varphi_1\tilde{T}_1 + (1 - \varphi_1)\tilde{T}_2$, $P^* = \varphi_1P_1^* + (1 - \varphi_1)P_2^*$, where φ designates the volume fraction, r_1 and r_2 the number of chain segments per molecule, and v^* the core volume per segment, and the subscripts 1 and 2 refer to solvent and polymer, respectively.[11]

We start with the general relation

$$(\partial V/\partial x_2) = \bar{v}_2 - \bar{v}_1 = \tilde{V}(\partial V^*/\partial x_2) + V^*(\partial \tilde{V}/\partial x_2) \quad (1)$$

where $\bar{v}_2$ and $\bar{v}_1$ are the partial molar volumes of polymer and solvent, respectively, and x_2 is the mole fraction of polymer.

According to corresponding states theory, $\tilde{V}$ is an explicit function of $\tilde{T}$ and $\tilde{P}$ only and

$$\bar{v}_2 = \bar{v}_1 + \tilde{V}(\partial V^*/\partial x_2) + V^*[(\partial\tilde{V}/\partial\tilde{T})_{\tilde{P}}(\mathrm{d}\tilde{T}/\mathrm{d}x_2) - (P/P^{*2})(\partial\tilde{V}/\partial\tilde{P})_{\tilde{T}}(\mathrm{d}P^*/\mathrm{d}x_2)] \quad (2)$$

In dilute solution $(\mathrm{d}/\mathrm{d}x_2) = r(\mathrm{d}/\mathrm{d}\varphi_2)$, where $r = r_2/r_1$. We obtain for the partial molar volume of the polymer per segment, Q

$$Q \equiv \bar{v}_2/r_2 = \bar{v}_1/r_2 + v^*\tilde{V}[(r_2 - r_1)/r_2] + (V^*/r_1)(\beta' - \alpha') \quad (3)$$

where

$$\alpha' = (\tilde{T}_1 - \tilde{T}_2)(\partial\tilde{V}/\partial\tilde{T})_{\tilde{P}}$$

$$\beta' = (P_1^* - P_2^*)(P/P^{*2})(\partial\tilde{V}/\partial\tilde{P})_{\tilde{T}}$$

In dilute polymer solution $(x_1 = 1)$

$$V^* = v^*r_1(1 + \varphi_2)$$

and

$$Q = \bar{v}_1/r_2 + v^*\{[1 - (r_1/r_2)]\tilde{V} + (1 + \varphi_2)(\beta' - \alpha')\} \quad (4)$$

If $r_2 \gg r_1$ (a true polymer–solvent system),

$$Q = v^*[\tilde{V} + (1 + \varphi_2)(\beta' - \alpha')] \quad (5)$$

Equation 5 allows one to calculate the magnitude of the partial molar volume per segment, Q, from the FOV equation and gives an insight into the origin of any abnormal behavior of the partial molar volume.[1] We note the dependence of Q on α' and β', parameters depending on the reduced thermal expansion coefficient and on the reduced compressibility, respectively, and on the difference in reduced properties of the two pure components. It is primarily the large value of α', which at sufficiently high $\tilde{V}$ causes the partial molar volume to be substantially less than the molar volume and, in extreme cases, to go negative. A direct experimental test of eq 5 would only be possible for binary supercritical mixtures of homologues containing a component of high molecular weight, and sufficiently accurate data are unavailable for such systems. However, for supercritical ethane–*n*-heptane mixtures, eq 5 gives results which are qualitatively similar to those obtained by direct calculations based on the FOV equation,[1] the differences between the two being associated with the long-chain approximation underlying eq 5. Such direct calculations based on the FOV equation were shown to be largely successful (but see below) for C_2–C_7 mixtures, and this provides some measure of validity for eq 5.

We have calculated Q for the binary supercritical paraffin mixtures C_5–C_∞ and C_2–C_∞ at pressures just sufficient to assure a single supercritical phase,[9] using reference parameters recommended by Patterson and Delmas for ethane and *n*-pentane[7] and by Orwoll and Flory for polyethylene.[8,12] These parameters are listed in Table I, and the results, obtained by computer, using an iteration method to solve for $\tilde{V}$,[1] are shown in Table II.

One concludes that the partial molar volume can be significantly smaller than the molar volume in supercritical C_5–C_∞ mixtures (pressure of the order of 100 atm), but does not differ greatly from the molar volume in C_2–C_∞ mixtures (pressures above 1000 atm). Thermodynamic and kinetic anomalies of the type considered do therefore not appear to play a significant role in the bulk homopolymerization of ethylene carried out at pressures in the neighborhood of 2000 atm, contrary to a suggestion made earlier.[2] We believe that the values of Q calculated represent reasonable approximations of the correct partial molar volume, in spite of the rather low densities (high $\tilde{V}$), even in the C_5–C_∞ mixtures where the physical assumptions commonly associated with the FOV equation are no longer satisfied; in partial support of that statement one may cite the fact that the FOV equation gives a fair first-order approximation of molar volume data in C_2–C_7 mixtures at even lower densities than those of Table II.[1]

Table I
Reference Parameters[7,8,a]

	Ethane	*n*-Pentane	Polyethylene
T^* °K	2674	4166	7539
P^*, atm	3218	4037	4542

[a] $v^* = 14.50$ cm³ per mol of segments. $r_i = n_i + 1$, where n_i is the number of carbon atoms per molecule.

Table II
Partial Molar Volume of Polymer per Mole of Segments, *Q*, and Related Parameters

	C_5–C_∞ at 180°C and 120 atm[a]				C_2–C_∞ at 150°C[b] and 1180 atm[b]			
ϕ_2	$\tilde{V}$	α'	β'	$Q \equiv \bar{v}_2/r_2$, cm³	$\tilde{V}$	α'	β'	$Q \equiv \bar{v}_2/r_2$, cm³
0.00	1.81	1.15	0.028	10.0	1.52	0.46	0.133	17.3
0.01	1.80	1.12	0.027	10.0	1.52	0.46	0.131	17.2
0.02	1.79	1.10	0.026	10.1	1.51	0.46	0.129	17.1
0.05	1.75	1.02	0.023	10.2	1.50	0.46	0.124	16.7
0.10	1.71	0.92	0.019	10.3	1.49	0.46	0.116	16.1
Volume of polymer per mole of segments $(V_2/r_2) = 18.2$ cm³[c]					Volume of polymer per mole of segments $(V_2/r_2) = 16.8$ cm³[c]			

[a] Corresponds to estimated maximum pressure on critical locus.[9] [b] Near the critical locus.[9] [c] These values, calculated from the FOV equation as $14.50\tilde{V}$, are in good agreement with specific volume data from the literature.[10]

As shown in Table II, the partial molar volume of the less volatile component, calculated according to eq 5 for the polymer-containing mixtures, shows only a very weak dependence on composition. A strong dependence is found experimentally and calculated by direct application of the FOV and Redlich–Kwong (RK) equations of state for the supercritical C_2–C_7 mixtures.[1] In fact, both equations predict sharp minima in $\bar{v}_2$ when plotted against composition over certain ranges of temperature and pressure. Experimentally, the existence of such minima could not be substantiated.[1] Analysis of the data according to eq 5 shows that the minima are associated with maxima in the reduced thermal expansion coefficient when plotted vs. reduced temperature according to the FOV equation at high reduced temperature, where that equation can certainly not be expected to provide an adequate representation of the temperature dependence of α'. This throws considerable doubt on the existence of minima in $\bar{v}_2(x_2)$ in C_2–C_7 mixtures.[1]

In summary, we believe eq 5 allows one to make useful estimates of the partial molar volume of a polymer in dilute supercritical mixtures, where it may differ substantially from the molar volume. Since Q depends on the derivatives of the reduced volume α' and β', and since the correct representation of these quantities places additional demands on the equation of state, it is clear that eq 5 will become increasingly unsatisfactory at increasing values of $\tilde{V}$, where the magnitude of α' approaches or exceeds that of $\bar{V}$. The analysis leading to eq 5 also shows that calculations of the composition dependence of the partial molar volume based on simple equations of state such as the FOV and RK equations must be interpreted with particular caution where such equations predict sharp minima in $\bar{v}_2$, as they do for C_2–C_7 mixtures.

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(12) We are not concerned here with any inconsistencies between the reference values recommended by these two sets of investigators because of the approximate nature of these calculations.

Surface Effects of the Four-Choice Cubic Lattice

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Recently, Mark and Windwer[2] and Lax[3-6] have investigated properties of self-avoiding chains generated in the presence of a barrier. One of us has shown[4-6] that the chain partition function for surface restricted walks can be represented by an equation of the following form

$$C_N{}^{\mathrm{s}} \sim \mu_{\mathrm{s}} N^{\alpha_{\mathrm{s}}} \qquad N \to \infty \tag{1}$$

where $C_N{}^{\mathrm{s}}$ is the walk count in the presence of a barrier, α_{s} is the long-range index of surface chains, and μ_{s} is the effective coordination number. A similar expression exists for bulk generated chains,[7] namely,

$$C_N{}^{\mathrm{b}} \sim \mu_{\mathrm{b}} N^{\alpha_{\mathrm{b}}} \qquad N \to \infty \tag{2}$$

where $C_N{}^{\mathrm{b}}$ is the walk count in the absence of a barrier, α_{b} is now the long-range index in bulk, and μ_{b} is the effective coordination number. The questions naturally arise: is α_{s} a dimensionally independent parameter as has been found for α_{b}; is μ_{s} identical in magnitude with μ_{b} or do they differ by some small number; what is the order of magnitude for the surface contribution to α_{s} defined as α^0? Lax,[4] in particular, estimated the magnitude of α^0, the difference between the value for the long-range index α_{s} of surface chains and that of the long-range index α_{b} of bulk generated chains. Estimates for α^0 are obtained by plotting $\alpha_N{}^0$ values from eq 3 vs. $1/N$ and extrapolating to $1/N = 0$

$$\alpha_N{}^0 \sim [N/(\mu_{\mathrm{s}}/\mu_{\mathrm{b}})][\rho_{N+1}/\rho_N - \mu_{\mathrm{s}}/\mu_{\mathrm{b}}] \tag{3}$$

Table I
A List of the Number of Self-Avoiding Walks of Size N ($C_N{}^{\mathrm{b}}$) in the Absence of a Solid Surface (Bulk Values) and the Number of Such Walks ($C_N{}^{\mathrm{s}}$) (Surface Values) in the Presence of a Solid Barrier on the Four-Choice Cubic Lattice

N	$C_N{}^{\mathrm{b}}$	$C_N{}^{\mathrm{s}}$
4	360	192
5	1,368	692
6	4,992	2,388
7	18,408	8,324
8	67,320	28,936
9	247,152	101,704
10	900,552	356,600
11	3,290,328	1,257,044
12	11,965,752	4,420,548
13	43,588,848	15,595,912
14	158,264,544	54,980,576

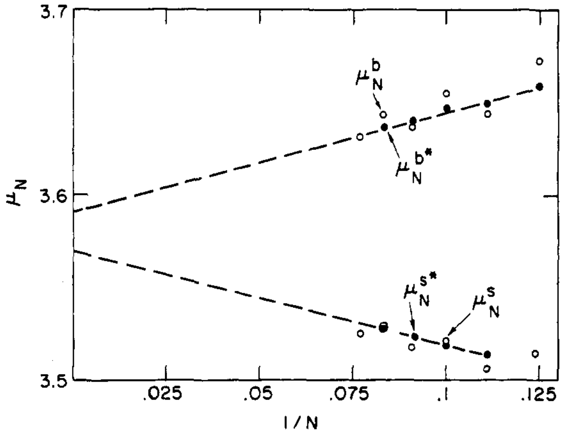

Figure 1. Plot of $\mu_N{}^{\mathrm{s}}$ and $\mu_N{}^{\mathrm{b}}$ and average values. $\mu_N{}^{\mathrm{s*}} \equiv (\mu_N{}^{\mathrm{s}} + \mu_{N+1}{}^{\mathrm{s}})/2$, $\mu_N{}^{\mathrm{b*}} \equiv (\mu_N{}^{\mathrm{b}} + \mu_{N+1}{}^{\mathrm{b}})/2$ vs. $1/N$.

$$\alpha_N{}^{0*} = (\alpha_N{}^0 + \alpha_{N+1}{}^0)/2 \tag{4}$$

where $\rho_N \equiv C_N{}^{\mathrm{s}}/C_N{}^{\mathrm{b}}$. (This equation is an expansion for ρ_{N+1}/ρ_N neglecting terms higher than N^{-1}.)

We now report results for the magnitudes of μ_{s}, μ_{b}, α^0, and α_{s} from an analysis of data obtained from self-avoiding walks generated on the four-choice cubic lattice in the presence and absence of a solid barrier. Table I lists the data for $C_N{}^{\mathrm{s}}$ and $C_N{}^{\mathrm{b}}$. The values obtained for $C_N{}^{\mathrm{b}}$ agree with those computed from the ratio of $b_N/\langle d_N \rangle$ reported by Bellemans.[8]

Figure 1 is a plot of $C_{N+1}{}^{\mathrm{s}}/C_N{}^{\mathrm{s}}$ and $C_{N+1}{}^{\mathrm{b}}/C_N{}^{\mathrm{b}}$ vs. $1/N$. Extrapolating to $1/N = 0$ one obtains $\mu_{\mathrm{b}} \sim 3.591$ and $\mu_{\mathrm{s}} \sim 3.570$. These limiting estimates obtained from short walks differ by 0.02. Similar behavior was reported by Lax[3] for the diamond lattice. The question as to whether or not this difference persists for longer chains still remains to be clarified. If one assumes such differences are not significant (i.e., $\mu_{\mathrm{b}} \equiv \mu_{\mathrm{s}}$), one obtains the following values for $\alpha_N{}^{0*}$ from eq 3 and 4: $\alpha_8{}^{0*} = -0.3403$; $\alpha_9{}^{0*} = -0.3457$; $\alpha_{10}{}^{0*} = -0.3575$; $\alpha_{11}{}^{0*} = -0.3705$; $\alpha_{12}{}^{0*} = -0.3779$. Linear extrapolation of alternate pairs of $\alpha_N{}^{0*}$ values given above yield $\alpha_{9,11}{}^{0*} \to -0.480$ and $\alpha_{10,12}{}^{0*} \to -0.480$, respectively. This value is within the experimental error of that obtained for α^0 on the diamond lattice[4] and suggests that α^0 (as well as α_{s}) are long-range exponents which are solely dimensional dependent. Using the accepted value of $\alpha_{\mathrm{b}} = \frac{1}{6}$ one estimates $\alpha_{\mathrm{s}} \sim -0.313$.