even-type dimers at the isotropization is close to 0.6.

A lower (~0.5) value has been measured by Griffin, Sigaud, and Yoon[3] on DG10, which is a dimeric compound of even type. However, our measurements on this compound give order parameters very close to those found for even dimers Dn.

The order parameters of odd-type dimers and both even- and odd-type monomeric compounds are included in a band of values that, on the average, lay 0.1 below the even dimeric compounds. Extrapolation to $T = T_{NI}$ leads to a limiting value that is close to the Maier–Saupe limit.

A conclusive remark arises both from the experimental results and from the theoretical calculations: the coupling of two rigid molecular sections (either as such or as a part of a polymeric chain) via a conformationally flexible spacer tends to increase the nematic orientational order, as compared to the monomeric homologues, only when the spacer has an even number of atoms along the backbone chain, producing, as a consequence, an enhancement of the odd-even fluctuation of the order parameter. Although some available thermodynamic measurements may allow reasonable extrapolations, no significant direct experimental evidence is available as yet concerning the extent of the connection of this phenomenon with the stereochemical nature and length of the flexible spacer.

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Registry No. $\mathrm{CH_3(CH_2)_4COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_3CH_3}$, 65224-17-1; $\mathrm{CH_3(CH_2)_3COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_3CH_3}$, 65224-16-0; $\mathrm{CH_3(CH_2)_4COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_7COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_4CH_3}$, 98585-84-3; $\mathrm{CH_3(CH_2)_4COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_{10}COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_4CH_3}$, 98585-86-5; $\mathrm{CH_3(CH_2)_4O\text{-}\mathit{p}\text{-}C_6H_4\text{-}COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}O(CH_2)_{10}O\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC\text{-}\mathit{p}\text{-}C_6H_4\text{-}O(CH_2)_4CH_3}$, 78352-90-6; $\mathrm{CH_3(CH_2)_4\text{-}COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}CH\text{-}C_6H_4\text{-}\mathit{p}\text{-}OOC(CH_2)_9COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_4CH_3}$, 98585-85-4; $\mathrm{CH_3(CH_2)_4COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_8COO\text{-}\mathit{p}\text{-}C_6H_4\text{-}C(CH_3){=}HC\text{-}\mathit{p}\text{-}C_6H_4\text{-}OOC(CH_2)_4CH_3}$, 98585-87-6.

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Notes

A Semiempirical Equation of State for Molten Polymers and Hydrocarbon Liquids

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In a previous paper,[1] we proposed a new expression for the free volume applicable to polymer and low molecular weight hydrocarbon mixtures. It was coupled with the well-known UNIFAC model[2] as the free volume term. The newly proposed UNIFAC-FV model was found to be successful to predict solubilities of various hydrocarbon gases and vapors in molten polystyrene, polypropylene, polyethylene, and polybutadiene[1,3] from the contributions of each group contained in the molecules.

In the present study, a semiempirical equation of state applicable to liquid states is derived from the partition function containing the free volume term mentioned above. The equation of state derived is applied to predict specific volumes of low molecular weight hydrocarbon liquids and molten polymers.

Partition Function and Equation of State

Details of derivation for the partition function have been previously reported.[1] In brief, the partition function Z has been derived based on the concept of Flory[4] and is given by the equation

$$Z = Z_{\mathrm{comb}}\left(\frac{v^*}{\Lambda^3}\right)^{crN}(\tilde{v}_{\mathrm{f}})^{crN}(q_{\mathrm{int}})^{rN} \times \exp\left\{\frac{s\eta rN\exp(0.3\tilde{v})}{2k\tilde{v}^{1.66}T^{1.23}}\right\} \quad (1)$$

where

$$\tilde{v}_{\mathrm{f}} = (\tilde{v}-1)\exp\left\{-\frac{18(\tilde{v}-1)^2 + 9(\tilde{v}-1) + 2}{6(\tilde{v}-1)^3}\right\} \quad (2)$$

$$\tilde{v} = v/v^* \quad (3)$$

The functional form of Z was empirically determined by using the PVT and heat of vaporization data of low molecular weight hydrocarbons. In the above equations, Z_{comb} is the combinatorial partition function, v^* is the hard-core volume per segment, Λ is the de Broglie wavelength, c is the one-third external degrees of freedom per segment, r is the number of segments per molecule, and N is the number of molecules. Further, $\tilde{v}_{\mathrm{f}}$ is the reduced free volume, q_{int} is the partition function arising from internal rotation and vibration degrees of freedom, s is the number of intermolecular contact sites per segment, η is a constant characterizing the energy of interaction for a pair of neighboring sites and having the dimensions of $JK^{0.23}$, $\tilde{v}$ is the reduced volume defined by eq 3, v is the molar volume, v^* is the hard-core volume per mole, k is the Boltzmann constant, and T is the temperature.

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Table I
Group Hard-Core Volumes and the One-Third External Degrees of Freedom[1]

group		$v^*_k \times 10^6$,[a] $m^3 \cdot mol^{-1}$	C_k[b]
CH_3	end group of hydrocarbon chain	13.7	0.214
CH_2	middle group in hydrocarbon chain	10.2	0.032
$CH(CH_3)$	middle group in hydrocarbon chain	20.4	0.047
$C(CH_3)_2$	middle group in hydrocarbon chain	30.7	0.051
ACH	aromatic hydrocarbon group	8.1	0.083
$ACCH_3$	aromatic–aliphatic hydrocarbon group	19.2	0.083
ACCH	aromatic–aliphatic hydrocarbon group	12.3	

[a] Calculated from Bondi's van der Waals volumes,[5] $v^* = \sum_k \nu_k v^*_k$. [b] $C = \sum_k \nu_k C_k$, where ν_k is the number of groups k in the molecule.

Table II
Characteristic Parameters

component	$v^* \times 10^6$, $m^3 \cdot mol^{-1}$	C	T^*, K	$P^* = CRT^*/v^*$, MPa
n-hexane	68.2	0.556	4600	312
n-heptane	78.4	0.588	4900	305
n-octane	88.6	0.620	5200	302
n-nonane	98.8	0.652	5400	296
benzene	48.6	0.498	5100	434
toluene	59.7	0.498	5500	381
m-xylene	70.8	0.498	5900	345

Table III
Interaction Parameters for Aliphatic Hydrocarbons

component	Q[a]	$\epsilon = s\eta r/2kQ$, $K^{1.23}$
n-hexane	3.856	4615
n-heptane	4.396	4627
n-octane	4.936	4674
n-nonane	5.476	4641

[a] UNIFAC area parameter[7] (dimensionless quantity).

An equation of state in reduced form can be obtained from the partition function based on a standard statistical thermodynamic treatment.

$$\tilde{P} = \tilde{T}\frac{\tilde{v}^3}{(\tilde{v}-1)^4} - \frac{1}{\tilde{T}^{0.23}}\exp(0.3\tilde{v})\frac{1.66 - 0.3\tilde{v}}{\tilde{v}^{2.66}} \qquad (4)$$

where

$$\tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{CRT^*} \qquad (5)$$

$$\tilde{T} = \frac{T}{T^*} = T\left(\frac{2Ck}{s\eta r}\right)^{1/1.23} \qquad (6)$$

In eq 5, R is the gas constant and C is the one-third external degrees of freedom per molecule. The values of v^* and C can be obtained by summing up the group parameters previously determined.[1] They are shown in Table I.

Results and Discussion

The interaction parameter appearing in eq 6, $s\eta r/2k$, is difficult to predict. Therefore, it was evaluated from the saturated volume data of pure hydrocarbons.[6] Table II lists the parameters T^* and P^* for aliphatic and aromatic hydrocarbons. As shown in Table III it seems that the interaction parameter per surface area, $\epsilon = s\eta r/2kQ$, is almost identical for a series of aliphatic hydrocarbons and the average value of ϵ is 4640. Figure 1 shows the calculated and experimental specific volumes of *n*-nonane[8] as an example. The parameters used for *n*-nonane are $v^*_{sp} = 0.770 \times 10^{-3}$ $m^3 \cdot kg^{-1}$, $T^* = 5399$ K ($\epsilon = 4640$), and $P^* = 296.1$ MPa, where v^*_{sp} is the hard-core volume per kg. The specific volume of *n*-nonane can be calculated with good agreement.

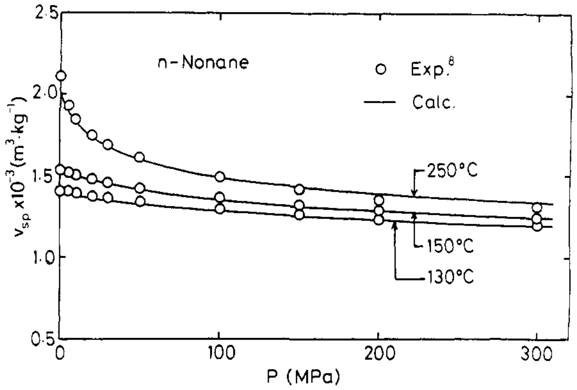

Figure 1. Specific volumes of *n*-nonane.

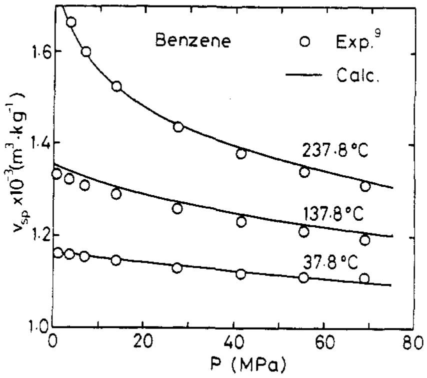

Figure 2. Specific volumes of benzene.

Table IV
Interaction Parameters for Aromatic Hydrocarbons

component	Q_{al}[a]	Q_{ar}[b]	$\epsilon_{ar} = (s\eta r/2k - 4640Q_{al})/Q_{ar}$, $K^{1.23}$
benzene	0.0	2.400	7543
toluene	0.848	2.120	7509
m-xylene	1.696	1.840	7487

[a] UNIFAC area parameter for the aliphatic hydrocarbon group[7] (dimensionless quantity). [b] UNIFAC area parameter for the aromatic hydrocarbon group[7] (dimensionless quantity).

Table IV shows the values of ϵ_{ar}, defined as $\epsilon_{ar} = (s\eta r/2k - 4640Q_{al})/Q_{ar}$ for aromatic hydrocarbons, where Q_{al} means the area of the aliphatic carbon group attached to the aromatic carbon group and Q_{ar} denotes the area of the aromatic carbon group ($=Q - Q_{al}$). From this table, the averaged value of ϵ_{ar} is obtained as 7510. For example, the parameters of benzene can be calculated as $v^*_{sp} = (48.6 \times 10^{-6})/(78.114 \times 10^{-3}) = 0.6222 \times 10^{-3}$ $m^3 \cdot kg^{-1}$, $T^* = (7510 \times 2.40/0.498)^{1/1.23} = 5084$ K, and $P^* = 0.498 \times 8.314 \times 5084/48.6 \times 10^{-6} = 433.1$ MPa. As shown in Figure 2, the calculated results are in good agreement with the experimental data.[9]

The equation of state can be applied to calculate the specific volumes of molten polymers. Figure 3 shows the calculated results for specific volumes of low-density polyethylene and experimental data.[10] The specific volume of low-density polyethylene at 23 °C is obtained as 1.0996 $\times 10^{-3}$ $m^3 \cdot kg^{-1}$ by interpolation of the data. Then the number of CH_3 groups per hundred carbon atoms can be estimated as 4.2 on the basis of the equation of Sperati et al.[11] The parameters of low-density polyethylene are thus obtained as $C = 0.214 \times 0.042 + 0.032 \times (1 - 0.042) = 0.03964$, $Q = 0.848 \times 0.042 + 0.540 \times (1 - 0.042) = 0.5529$,

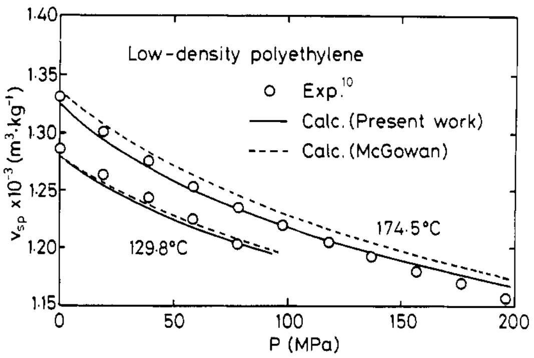

Figure 3. Specific volumes of low-density polyethylene.

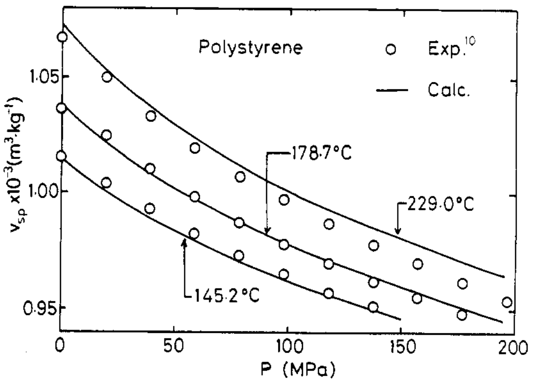

Figure 4. Specific volumes of polystyrene.

$v^*_{sp} = \{13.7 \times 10^{-6} \times 0.042 + 10.2 \times 10^{-6} \times (1 - 0.042)\}/\{15 \times 10^{-3} \times 0.042 + 14 \times 10^{-3} \times (1 - 0.042)\} = 0.7369 \times 10^{-3}$ m^3·kg^{-1}, $T^* = (4640 \times 0.5529/0.03964)^{1/1.23} = 8155$ K, and $P^* = 0.03964 \times 8.314 \times 8155/\{13.7 \times 10^{-6} \times 0.042 + 10.2 \times 10^{-6} \times (1 - 0.042)\} = 259.7$MPa, where Q is the UNIFAC area parameter.[7] For comparison, the results calculated with McGowan's equation[12] ($21P'/M' = 59.8$, $T'_c = 403$ K) are also shown in Figure 3. The value of T'_c is determined to give a good fit for the experimental specific volumes. It seems the present results are slightly better.

For the case of polystyrene, it is difficult to estimate the one-third external degrees of freedom per repeating unit. As shown in Table I, the value of C_k for the end group of the hydrocarbon chain (CH_3) is much larger than that for the middle group in the hydrocarbon chain ($CH(CH_3)$ or $C(CH_3)_2$). Therefore, it is reasonable to consider that the external degrees of freedom for the phenyl group attached to the main chain is smaller than that for benzene. The one-third external degrees of freedom per repeating unit was determined as 0.25 by fitting the calculated results to specific volumes of polystyrene. The values of the parameters for polystyrene are calculated as $v^*_{sp} = (10.2 \times 10^{-6} + 8.1 \times 10^{-6} \times 5 + 12.3 \times 10^{-6})/104.152 \times 10^{-3} = 0.6049 \times 10^{-3}$ m^3·kg^{-1}, $T^* = \{(4640 \times 0.768 + 7510 \times 2.120)/0.25\}^{1/1.23} = 9485$ K, $P^* = 0.25 \times 8.314 \times 9485/(10.2 \times 10^{-6} + 8.1 \times 10^{-6} \times 5 + 12.3 \times 10^{-6}) = 312.9$ MPa. The results calculated with these parameters are in good agreement with the experimental data[10] as shown in Figure 4. It is noted that application of the present equation of state is limited to liquid states.

Summary

A semiempirical equation of state has been developed to predict specific volumes of molten polymers and low molecular weight hydrocarbon liquids. The values of the parameters needed in the prediction can be obtained by summing up group parameters alone. The group parameters are reported for aliphatic and aromatic hydrocarbons. The specific volumes of molten polymers such as low-density polyethylene and polystyrene can also be calculated by use of the group parameters. However, the one-third external degrees of freedom per repeating unit for polystyrene should be adjusted to obtain good results.

Registry No. Polyethylene (homopolymer), 9002-88-4; polystyrene (homopolymer), 9003-53-6; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; benzene, 71-43-2; toluene, 108-88-3; *m*-xylene, 108-38-3.

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Activation of Epoxide Polymerization under Ultraviolet Radiation

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Conversion of epoxide to polymer was found to increase significantly under UV irradiation in the presence of a tris(β-diketonato)aluminum (Al-I) and triphenylsilanol, which we have already described.[1] Also we have reported[2-4] the initiation mechanism of the polymerization of epoxides by these catalysts.

Results obtained with cyclohexene oxide and three aluminum-based catalysts[6] are shown in Figure 1. In the case of tris(2,4-pentanedionato)aluminum ($Al(acac)_3$) and triphenylsilanol catalyst, conversion to polymer under UV irradiation was about 3-5 times higher than that in the dark. The temperature change of the polymerization system caused by UV radiation with a mercury lamp was negligible.

An increase in polymer conversion under UV irradiation was also observed when the Al-I complexes tris(1,1,1-trifluoro-2,4-pentanedionato)aluminum ($Al(tfp)_3$) and tris(2,6-dimethyl-3,5-heptanedionato)aluminum ($Al(dmh)_3$) were employed (Figure 1). The increase was remarkable when an aluminum complex substituted with an electron-donating group on the carbon bonded to the carbonyl carbon, such as $Al(dmh)_3$, was used.

The molecular weight of the polymer polymerized with ($Al(acac)_3$)/triphenylsilanol catalyst for 60 min under the same conditions shown in Figure 1 was measured by gel permeation chromatography with a Toyo Soda Type 801 apparatus (column constitution, G-2000H$_8$, G-2000H$_8$, G-3000H$_8$, and G-4000H$_8$ (polystyrene gel)) by elution with THF at 40 °C. Calibration was carried out with standard polystyrene mixtures. M_n and M_w, which were 13 000 and 35 000, respectively, in the dark, increased to 21 000 and

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