characterized polyethylene; to Dr. J. M. G. Cowie, National Research Council, Canada, for high molecular weight α-methylstyrene polymers; to Mr. J. A. Reed, Phillips Petroleum Co., for poly(1-butene); and to Dr. F. E. Karasz, General Electric Co., for the polystyrenes and two polymers, PPO and Lexan, used in this work. This study was partially supported by a Robert A. Welch Foundation research grant.

Correlation Procedures for Estimating the Enthalpies of Vaporization, Formation, and Polymerization and Certain Physical Properties of α-Olefin Polymers

R. M. Joshi, B. J. Zwolinski, and C. W. Hayes

Department of Chemistry, Texas A&M University, College Station, Texas.

Received September 7, 1967

ABSTRACT: The Somayajulu–Zwolinski generalized bond-energy scheme developed for low molecular weight isomeric alkanes has been extended to 15 olefinic polymer structures for estimating their enthalpies of formation and enthalpies of polymerization. The agreement with available experimental data is quite satisfactory, provided that due allowance is made for the structural energy differences arising from tacticity of the α-olefin polymers. The Tatevskii procedure, which successfully correlates several physical properties of hydrocarbons, was also applied to the olefin polymers for calculating the molal volume (densities), molal refraction (and refractive indices), and enthalpy of vaporization of a polymer repeat unit. The predicted densities, while internally consistent, are generally 1–7% high, whereas the sparse experimental values vary among themselves by 1–10%. The usefulness of these estimated molal volumes in calculating volume changes in polymerizations and for predicting effects of pressure for certain polymeric systems is noted. The calculated refractive indices show better agreement within 2%. The Greenshields–Rossini bond-energy procedure, although very precise for lower isomeric alkanes, was found to be inapplicable for estimating physicochemical properties of long-chain branched polyolefins.

In recent years empirical and semiempirical bond-energy schemes have proved quite successful[1] in predicting physical and thermodynamic properties such as molal refraction, density, boiling point, enthalpies of vaporization and of formation, etc., of paraffinic hydrocarbons, within a precision attainable experimentally. To our knowledge no systematic application of these procedures has been made for predicting similar properties for the hydrocarbon polymers except for a few occasional calculations[2] such as the enthalpy of polymerization. Poly(α-olefins) offer an excellent class of polymers to test the applicability and effectiveness of the various bond-energy and group-contribution procedures for predicting their physical and thermodynamic properties. The experimental data on the properties of these hydrocarbon polymers are rather meager at present; however, it is very rapidly accumulating and these relatively simple polymers offer an ideal testing ground for determining the effectiveness of correlation procedures in evaluating, correlating, and extending experimental data.

The enthalpy of formation and the enthalpy of vaporization (hypothetical) of a polymer segment are important thermodynamic quantities often required in interpretations of polymolecular phenomena such as intermolecular entanglement,[3] chain stiffness,[4] glass transition,[4,5] cohesive energy density,[6] etc. The enthalpy of vaporization of a polymer segment is not an experimentally measurable quantity, for obvious reasons, and only an estimated value is possible. The enthalpies of formation for the condensed phase can be accurately determined from precise heats of combustion measured in bomb calorimetry and such a program for obtaining the standard enthalpies of formation of certain classes of polymers including the α-olefin polymers has been initiated in our laboratory.[7] For these thermal data to be truly useful, it is necessary to define the condensed phase of the polymer more rigorously and at the same time to reduce the enthalpy of formation data to the standard ideal gas phase at 25°. Only then are we in a position to correlate energies with the structural features of the polymer segment. To this end, the abstract quantity, the standard enthalpy of vaporization, is absolutely necessary. Furthermore one requires an experimental estimate of the degree of crystallinity, the heat of fusion, and the glass enthalpy of the amorphous state, all of which are associated with the so-called condensed (c) phase.

---

[1] (a) B. J. Zwolinski and R. C. Wilhoit, *Proc. Am. Petrol. Inst.*, **46**, 125 (1966); (b) G. R. Somayajulu and B. J. Zwolinski, *J. Phys. Chem.*, **70**, 3498 (1966); (c) G. R. Somayajulu, A. P. Kudchadker, and B. J. Zwolinski, *Ann. Rev. Phys. Chem.*, **16**, 213 (1965); (d) H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **17**, 264 (1963).

[2] (a) W. M. D. Bryant, *J. Polymer Sci.*, **A2**, 4643 (1964); **2**, 547 (1947); (b) F. S. Dainton and K. J. Ivin, *Quart. Rev.* (London), **12**, 61 (1958); (c) J. R. Schaefgen, *J. Polymer Sci.*, **38**, 549 (1959).

[3] R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).

[4] R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

[5] N. L. Zutty and C. J. Whitworth, *J. Polymer Sci.*, **B2**, 709 (1964).

[6] E. E. Walker, *J. Appl. Chem.* (London), **2**, 470 (1952).

[7] R. M. Joshi and B. J. Zwolinski, "Vinyl Polymerization," Vol. 1, Part I, G. E. Ham, Ed., Marcel Dekker, New York, N. Y., 1966, Chapter 8, p 445.

The enthalpy of fusion may be estimated calorimetrically through techniques such as the differential thermal analysis (DTA), while the glass enthalpy of polymer[8] below its glass transition temperature can either be computed from calorimetric specific heat–temperature data or estimated from the heat of mixing with a θ solvent. The third important derived thermochemical quantity often required for a precise understanding of the polymerization equilibrium is the enthalpy of polymerization. Large amounts of data from reaction calorimetry are currently available on the enthalpies of polymerization. Unfortunately most of the data involve nonstandard, ill-defined, "condensed" phases of the polymer and need reduction to either the ideal gas phase at the standard thermodynamic temperature of 298.15°K or to a "normal" liquid at the standard temperature.[7] Such a reduction of the present data is not feasible in most cases for lack of reliable specific heat and other thermal data.

Choice of Correlation Procedures

The choice of a correlation procedure for interpolating or extrapolating macroscopic properties for small molecules as a function of thermodynamic variables such as temperature and pressure is classically well defined. The choice of a molecular structural correlation procedure for interpolating and extrapolating structurally among a closely related group of compounds is theoretically less clearly defined. Our initial approach utilizing precise correlation procedures developed for homologous series proved to be ineffective for estimating properties of hydrocarbon polymers. Either the correlation functions converged too rapidly or lack of accurate data on *n*-mers such as trimers, tetramers, and pentamers kept us from fully testing the applicability of these procedures.

The problem is simplified if we regard the α-olefinic polymers to be highly branched isomeric alkanes. In the past dozen years,[1,9,10] reliable correlation procedures have been developed for coping with the subtle differences in properties arising from the shifting and/or addition of methyl and other alkyl groups to a carbon skeleton. The final choice of the correlation procedure was dictated by the following criteria: (1) to be highly precise and accurate for predicting bulk properties for isomeric alkanes within the errors of measurements, (2) to be sufficiently flexible so that physical properties, such as molal volume and molal refraction, and also thermodynamic properties, such as enthalpies of vaporization and formation, can be equally well estimated within the same phenomenological framework.

The following bond-energy procedures which meet these criteria quite well for isomeric alkanes were chosen for estimating the properties of hydrocarbon polymers. Briefly they may be described as follows.

(1) Tatevskii's group-contribution procedure,[11] developed by Tatevskii and his collaborators over a period of years, assumes that molal properties are additive, representing the summation of various bonds and groups constituting the molecule. For the paraffinic hydrocarbons, the contributions of the ten different types of C_i–C_j bonds and the four C_j–H type of hydrogen bonds were defined. The 14 parameters arising from these types of bonds were reduced to nine by recognizing from stoichiometry the interrelationships between the number and types of carbon atoms and their associated hydrogens. Several physicochemical properties such as the molal volume, the molal refraction, and the enthalpies of vaporization and formation were successfully correlated with the types of bonds and found to obey the simple, nine-parameter, additivity scheme in good agreement with experiment.

(2) Somayajulu–Zwolinski Generalized Nonbonded Steric Interaction Procedure. This procedure is an extension of methods developed by Zahn, Allen, and Skinner[1,12,13] for specifically taking into account the variation of bond energies in paraffinic hydrocarbons in terms of nonbonded steric interactions. In correlating standard enthalpies of association or formation for the ideal gaseous state the basic sum of the bond energies of C_i–H and C_i–C_j bonds is corrected for the interaction contribution calculated from the number and type of interactions and from geometrical weighting parameters denoting energetically the magnitude of each interaction. This phenomenological procedure is considered to be fundamentally a bit more realistic since it defines theoretically the possibility of computing in the future bond–bond interaction parameters quantum mechanically and independently from first principles through a procedure such as the Brown's LCBO theory.[12,13] This procedure has also been successfully applied to physical properties of liquid alkanes.

(3) The Greenshields–Rossini Isomeric Variation Method.[10] The difference between the physical property of an isomeric hydrocarbon and of its corresponding normal straight-chain alkane with the same number of carbons is calculated with the help of a set of empirical equations, the coefficients of which have been computed from a least-square fit of selected experimental data for each property. The molecular structural parameters are evaluated for an isomer and its normal analog and the *difference* is employed in the appropriate empirical equation. The isomeric variation increment thus calculated is added to the basic property of the normal alkane as found in the API Research Project 44 tables.[10,13]

Further discussions of the merits of these three correlation procedures have appeared in recent reviews by Skinner and Pilcher[1] and Somayajulu, Kudchadker, and Zwolinski.[1]

Extension of Isomeric Alkane Correlation Procedures to α-Olefin Polymers

Polymers of all methyl-substituted ethylenes as well as a few other experimentally realized α-olefin polymers, such as the monosubstituted alkyl ethylenes,

---

[8] S. Bywater, *Makromol. Chem.*, **52**, 120 (1962); **86**, 116 (1965).

[9] J. D. Cox, *Tetrahedron*, **18**, 1337 (1962); **19**, 1175 (1963).

[10] J. B. Greenshields and F. D. Rossini, *J. Phys. Chem.*, **62**, 271 (1958).

[11] V. M. Tatevskii, V. A. Benderskii, and S. S. Yarovoi, "Rules and Methods for Calculating the Physico-Chemical Properties of Paraffinic Hydrocarbons," Pergamon Press Ltd., London, 1961.

[12] R. D. Brown, *J. Chem. Soc.*, 2615 (1953).

[13] G. R. Somayajulu and B. J. Zwolinski, *Trans. Faraday Soc.*, **62**, 2327 (1966).

Table I

PHYSICAL AND THERMODYNAMIC PROPERTIES OF OLEFINIC MONOMERS AT 25°[a] AND THE PREDICTED PROPERTIES OF THE POLYMERS

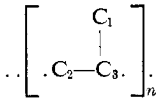
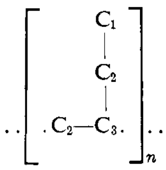
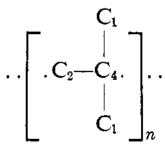
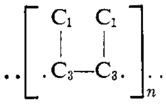
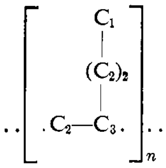
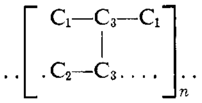
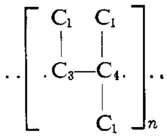
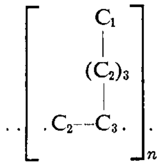
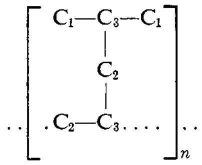
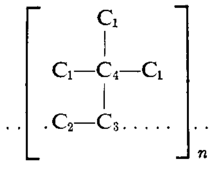
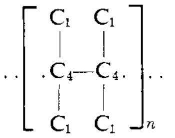
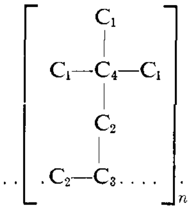
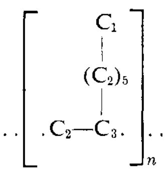
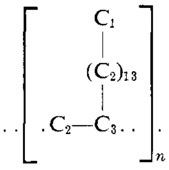
			Tatevskii's scheme[d]				Somayajulu and Zwolinski scheme[b] Structural parameters			
No.	Olefin and poly(olefin)	Polymer structure[b]	$V°$(l), ml/mol	$R°$(l), ml/mol	$\Delta H_v°$(lg), kcal/mol	$-\Delta H_f°$(g), kcal/mol	m	l	$-\Delta H_f°$(g), kcal/mol	Exptl[c] $-\Delta H_f°$(g), kcal/mol
1.	Ethylene		73.06	...	(3.24)	−12.50				
	Poly(ethylene)	$\cdot\cdot[\cdot C_2{-}C_2\cdot]_n\cdot\cdot$	32.02	9.274	2.36	9.92	4	0	9.84	9.89
2.	Propylene		83.28	...	4.40	−4.88				
	Poly(propylene)	 $\cdot\cdot[\cdot C_2{-}C_3(C_1)\cdot]_n\cdot\cdot$	47.11	13.828	3.29	15.95	8	4	15.98	15.55
3.	1-Butene		95.29	...	4.81	0.03				
	Poly(1-butene)	 $\cdot\cdot[\cdot C_2{-}C_3(C_2C_1)\cdot]_n\cdot\cdot$	61.20	18.322	4.63	20.28	9	6	20.34	19.50
4.	2-Methyl-1-propene		95.44	...	4.92	4.04				
	Poly(2-methyl-1-propene)	 $\cdot\cdot[\cdot C_2{-}C_4(C_1)_2\cdot]_n\cdot\cdot$	61.60	18.362	3.96	22.76	15	36	17.32	17.11
5.	2-Butene	*cis*	91.17	...	5.29	1.67				
		trans	93.76	...	5.10	2.67				
	Poly(2-butene)	 $\cdot\cdot[\cdot C_3(C_1){-}C_3(C_1)\cdot]_n\cdot\cdot$	57.28	18.072	4.78	19.62	10	16	21.02	
6.	1-Pentene		110.39	24.868	6.09	5.00				
	Poly(1-pentene)	 $\cdot\cdot[\cdot C_2{-}C_3((C_2)_2C_1)\cdot]_n\cdot\cdot$	77.21	22.959	5.81	25.24	11	6	25.26	
7.	3-Methyl-1-butene		112.78	24.96	5.70	6.92				
	Poly(3-methyl-1-butene)	 $\cdot\cdot[\cdot C_2{-}C_3(C_3(C_1)_2)\cdots]_n\cdot\cdot$	75.75	22.864	5.68	25.76	13	12	25.96	
8.	2-Methyl-2-butene		106.75	24.97	6.47	10.17				
	Poly(2-methyl-2-butene)	 $\cdot\cdot[\cdot C_3(C_1){-}C_4(C_1)_2\cdot]_n\cdot\cdot$	68.67	22.432	5.15	24.57	15	60	18.82	
9.	1-Hexene		125.90	29.504	7.32	9.96				
	Poly(1-hexene)	 $\cdot\cdot[\cdot C_2{-}C_3((C_2)_3C_1)\cdot]_n\cdot\cdot$	93.22	27.596	6.99	30.20	13	6	30.18	
10.	4-Methyl-1-pentene		127.72	29.565	6.86	11.66				
	Poly(4-methyl-1-pentene)	 $\cdot\cdot[\cdot C_2{-}C_3(C_2C_3(C_1)_2)\cdots]_n\cdot\cdot$	94.22	27.656	6.58	31.90	16	8	31.96	
11.	3,3-Dimethyl-1-butene		129.89	29.599	6.36	14.15				
	Poly(3,3-dimethyl-1-butene)	 $\cdot\cdot[\cdot C_2{-}C_3(C_4(C_1)_3)\cdots]_n\cdot\cdot$	90.33	27.42	6.29	31.81	20	22	33.22	

TABLE I (*Continued*)

No. Olefin and poly(olefin)	Polymer structure[b]	Tatevskii's scheme[d]				Somayajulu and Zwolinski scheme[b]			Exptl[c]
		$V°(l)$, ml/mol	$R°(l)$, ml/mol	$\Delta H_v°(lg)$, kcal/mol	$-\Delta H_f°(g)$, kcal/mol	Structural parameters m	l	$-\Delta H_f°(g)$, kcal/mol	$-\Delta H_f°(g)$, kcal/mol
12. 2,3-Dimethyl-2-butene		119.64	29.609	7.78	15.91				
Poly(2,3-dimethyl-2-butene)	 $\cdots\left[\begin{array}{c} C_1\ \ C_1 \\ \vert\ \ \ \vert \\ \cdot C_4{-}C_4\cdot \\ \vert\ \ \ \vert \\ C_1\ \ C_1 \end{array}\right]_n\cdots$	75.02	26.604	5.86	27.74	18	96	19.32	
13. 4,4-Dimethyl-1-pentene	 $\cdots\left[\begin{array}{c} C_1 \\ \vert \\ C_1{-}C_4{-}C_1 \\ \vert \\ C_2 \\ \vert \\ \cdot C_2{-}C_3\cdots \end{array}\right]_n\cdot$	144.81	34.243	7.45	19.8				
Poly(4,4-dimethyl-1-pentene)		110.35	32.299	7.34	39.23	24	22	37.09	
14. 1-Octene	 $\cdots\left[\begin{array}{c} C_1 \\ \vert \\ (C_2)_5 \\ \vert \\ \cdot C_2{-}C_3\cdot \end{array}\right]_n\cdots$	157.86	38.79	9.70	19.82				
Poly(1-octene)		125.24	36.870	9.35	40.12	17	6	40.02	
15. 1-Hexadecene	 $\cdots\left[\begin{array}{c} C_1 \\ \vert \\ (C_2)_{13} \\ \vert \\ \cdot C_2{-}C_3\cdot\cdot \end{array}\right]_n\cdots$	289.63	75.922	19.14	59.23				
Poly(1-hexadecene)		253.32	73.966	18.35	79.80	33	6	79.38	

[a] "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Project 44, Thermodynamics Research Center, Texas A&M University, College Station, Texas (loose-leaf data sheets, extant, 1967). [b] Subscripts on C denote 1 = primary, 2 = secondary, etc.; hydrogen atoms not shown. [c] Experimental $\Delta H_f°(l) + \Delta H_v°$ (column 3). [d] For abbreviations, see Table II, footnote *c*.

were chosen for this study. The effectiveness of the three correlation procedures was explored for predicting specifically the following properties: (a) the thermodynamic properties such as the standard enthalpy of vaporization per monomole (hereafter referred to as mole) and the standard ideal gas enthalpy of formation per monomole, and (b) the physical properties such as the molal volume and molal refraction. The details of the extension of these correlation procedures to the hydrocarbon polymers is described below.

The application of Tatevskii's group-contribution scheme (TBY scheme)[11] is straightforward as shown by the following example of calculating the enthalpy of formation of poly(propylene) repeat unit which has one C_1–C_3 and two C_2–C_3 bonds. The corresponding parameters H_{ij} for these two types of bonds are −10.79 and −2.58 kcal/mol, respectively. For example, the enthalpy of formation in the standard ideal gas phase is given by eq 1. It may be noted that for a polymer

$$\Delta H_f°(\ldots C_2\text{–}\overset{\overset{\displaystyle C_1}{\vert}}{C_3}\ldots) = \sum H_{ij} = 2(-2.58) + 1(-10.79) = -15.95 \text{ kcal/mol} \quad (1)$$

segment to represent a polymer molecule, one extra (*e.g.*, C_2–C_3-type for polypropylene) carbon–carbon bond forming the chain has to be taken into account in the summation for a physical or thermodynamic property.

The same procedure and model of a polymer segment is required for calculating the structural parameters *n*, *m*, *l*, etc., defined by the Somayajulu and Zwolinski generalized procedure (SZ scheme),[13] namely, that there is one more carbon–carbon bond of the same type as that between the two carbons of the substituted ethylene and two less hydrogens in the repeat unit. Their general equation for the standard atomization enthalpy at 25°, as extended to olefin polymers (C_nH_{2n}), then becomes

$$E(C_nH_{2n}) = 2nE_0 + nE_{cc} + 3n_1\delta_1 + 4n_2\delta_2 + 3n_3\delta_3 + 2(m - 2n_2 - 3n_3)\delta_4 + ls \quad (2)$$

The standard enthalpy of formation $\Delta H_f°(g)$ is derived from eq 2 using the standard enthalpies of formation for C and H atoms which are 171.29 and 52.10 kcal/mol, respectively. The reader is referred to the original reference[13] for further details regarding the significance and the methods of calculating the structural parameters (n, m, l) and coefficients (δ_i, s) in this general equation. The weighting parameters, l and m, which are somewhat tedious to calculate, have been evaluated and are included in Table I along with the standard enthalpies of formation for the various polymers.

TABLE II

POLYMER PROPERTIES IN THE LIQUID STATE AT 25° AND DERIVED THERMODYNAMIC QUANTITIES FOR THE POLYMERIZATION REACTION

				Volume change on polymerization[c]		Heat of polymerization[c] $-\Delta H_p°(ll)$, kcal/mol		
						Predicted		
No.	Polymer	Density,[b,c] $d°(l)$, g/ml	Refractive index,[b,c] $n°_D(l)$	$-\Delta V_p°(ll)$, ml/mol	% monomer	Tatevskii, *et al.*	Somayajulu and Zwolinski	Exptl
1.	Poly(ethylene)	0.8762	1.4910	41.04	56.2	21.54	21.46	21.51
2.	Poly(propylene)	0.8933	1.4988	36.17	43.4	19.72	19.75	19.32
3.	Poly(1-butene)	0.9168	1.5106	34.09	35.8	20.07	20.13	19.29
4.	Poly(2-methyl-1-propene)	0.9109	1.5080	33.80	35.5	17.76	12.32	12.11
5.	Poly(2-butene)	0.9796	1.5436	35.12[a]	38.0[a]	17.44 (*cis*)	18.86 (*cis*)	...
						16.63 (*trans*)	18.05 (*trans*)	...
6.	Poly(1-pentene)	0.9084	1.5065	33.18	30.0	19.96	19.98	...
7.	Poly(3-methyl-1-butene)	0.9259	1.5156	37.02	32.8	18.82	19.02	...
8.	Poly(2-methyl-2-butene)	1.0213	1.5670	38.08	35.7	13.08	7.33	...
9.	Poly(1-hexene)	0.9028	1.5039	32.68	26.0	19.91	19.89	...
10.	Poly(4-methyl-1-pentene)	0.8933	1.4988	33.51	26.2	19.98	20.04	...
11.	Poly(3,3-dimethyl-1-butene)	0.9317	1.5191	39.56	30.4	17.62	19.00	...
12.	Poly(2,3-dimethyl-2-butene)	1.1219	1.6274	44.62	40.2	9.91	1.49	...
13.	Poly(4,4-dimethyl-1-pentene)	0.8898	1.4971	34.46	23.8	19.84	17.70	...
14.	Poly(1-octene)	0.8960	1.5006	32.62	20.7	19.95	19.85	...
15.	Poly(1-hexadecene)	0.8860	1.4958	36.31	12.5	19.78	19.36	...

[a] Mean of *cis*- and *trans*-2-butene. [b] Predicted values, see Table I, footnote *a*. [c] Abbreviations: H = enthalpy, V = molar volume, R = molar refraction, d = density, n_D = refractive index. ° indicates the standard state of temperature = 298.15°K and pressure = 1 atm. Subscripts denote the physical change: *e.g.*, f = formation from the elements, v = vaporization, p = polymerization. Letters in parentheses denote the phase or phases: *e.g.*, (g) = gas, (l) = liquid, (ll) = liquid to liquid, etc.

In extending the Greenshields–Rossini isomeric variation method (GR scheme)[10] to polymers, all the α-olefin polymers and polymers of α,β-substituted ethylene are considered as isomers of linear polyethylene with the same empirical formula, (C_nH_{2n}). The application of this procedure is straightforward once the terms which are a function of the Platt number (P_3) and the Wiener number (W) are determined for a polymer of infinite chain length. This was done graphically for appropriate properties of isomeric alkanes against the reciprocal of the degree of polymerization. The extrapolated Platt and Wiener functions gave unreasonable contributions to the properties of a polymer segment. Even though the GR procedure works exceedingly well for small isomeric alkanes, it was found to give unreasonable values for the predicted enthalpies of vaporization and formation as also other physical properties of hydrocarbon polymers.

Results and Discussion

Results of the application of the TBY scheme and the SZ scheme are shown in Tables I and II. The TBY procedure was found to be more effective than the SZ scheme and was used exclusively for predicting the physical properties of the hydrocarbon polymers such as molal volume, molal refraction, and the standard enthalpy of vaporization in Table I. Both procedures were used to correlate and predict the standard ideal gas enthalpies of formation and are compared with enthalpies of formation obtained in our laboratory[14] and elsewhere.[15]

Since physical properties such as molal volume, molal refraction, and standard enthalpies of vaporization are more or less governed by the over-all size of the molecule and the molecular surface forces, the TBY scheme should be adequate for a comparative study of such polymer properties by treating them as high molecular weight alkanes in the supercooled liquid state at 25°. The predicted hypothetical enthalpies of vaporization given in Table I for a polymer segment appear to be internally consistent for this closely related group of hydrocarbon polymers. Furthermore, once combined with experimental data for heats of fusion and heats of combustion for the first four α-olefinic polymers listed in Table I, very good agreement is obtained between experimentally derived and predicted standard enthalpies of formation in the ideal gaseous state.

The densities calculated from the predicted molal volumes for the supercooled liquid polymers at 25° are reported in Table II. Actual experimental room densities are reported in the literature[16,17] for six of the polymers, namely, polymers 1, 2, 3, 4, 6, and 10, as defined in Table II. These densities show wide variations in the values obtained by different investigators and a comparison with the predicted densities is difficult. For example, the following four density values are reported for polyethylene: 0.81, 0.85, 0.86, and 0.89 g/ml with a maximum deviation of some 5%. The predicted value is 0.876 g/ml. The predicted density of polyisobutylene, 0.911 g/ml, shows exceptionally good agreement with the experi-

---

(14) R. M. Joshi and B. J. Zwolinski, *Macromolecules*, **1**, 25 (1968).

(15) G. S. Parks, and H. P. Mosher, *J. Polymer Sci.*, **A1**, 1979 (1963).

(16) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," High Polymer Series Vol. XVII, Interscience Publishers, Inc., New York, N. Y., 1963, p 262.

(17) J. Brandrup and E. H. Immergut, "Polymer Handbook," Interscience Publishers, Inc., New York, N. Y., 1966.

mental value[17] of 0.91 g/ml in spite of its being a sterically hindered chain. In general where comparisons are possible the predicted density values appear to be high for these six polymers from 1 to 7%. This is not unexpected for it seems likely that long-chain molecules should not pack as closely as small hydrocarbon molecules and the experimental density should be slightly lower whether microvoids are important or not.

Since the calculated polymer densities are internally consistent for this group of polymers, they should prove useful on a relative scale for studying the effects of pressure on fusion equilibria and also on polymerization of monomers in the liquid state as discussed below. The predicted liquid refractive indices agree reasonably well with the experimental values for amorphous polyethylene[17] (1.52), polypropylene[18] (1.49), and polyisobutylene[19] (1.508).

From the experimental and estimated molal volumes, respectively, of pairs of monomers and polymers given in Table I, one is in a position to evaluate a most important thermodynamic datum, the molal volume change ($-\Delta V_p{}^\circ$(ll))[20] on polymerization of a monomer in the liquid state. These estimated values are given in Table II. Some understanding of the relative effects of high pressure in enhancing the polymerizability[21] of the various olefin monomers may be obtained from these estimated volume changes. In particular the polymerization of some 1,2-disubstituted ethylenes yet unachieved, such as polymers 8 and 12, should be facilitated by carrying out the preparations at higher pressures. Similarly a large pressure dependence should be expected in the polymerization of system 11, where a *t*-butyl substitution is closer to the chain backbone than in system 13.

The standard enthalpy of formation of a polymer segment for the ideal gaseous state is the most important property that can be predicted from bond-energy correlation procedures. Combining it with available enthalpy of formation data on monomers, we can calculate the enthalpy of polymerization for any substituted ethylene and predict its thermodynamic polymerizability. The enthalpies of formation and enthalpies of polymerization predicted for the first three polymers, polyethylene, polypropylene, and poly(1-butene), by both the TBY and SZ procedures agree closely with the experimental values; however, in the case of polyisobutylene the SZ scheme is definitely superior. Earlier studies[1] on low molecular weight isomeric alkanes revealed that the TBY scheme does not adequately take into account steric interactions. This is particularly evident in Table I in the standard enthalpies of formation of polymer segments containing tertiary and quaternary carbon atoms such as 2-methyl-2-butene and 2,3-dimethyl-2-butene. In general, the SZ scheme, owing to its systematic analysis of the type and number of all inductive and steric bond–bond interactions such as the "vicinal" 1–2 interaction and the "steric" 1–3 interaction extended up to four carbons, appears to predict more precisely the enthalpies of formation of olefin polymers. The predicted value ($\Delta H_f{}^\circ$(g) = -17.32 kcal/mole) for polyisobutylene, a well-known case of a highly hindered polymer chain, agrees well with the experimental -17.11 kcal/mol reported in a recent paper.[15] The difference of 0.2 kcal/mol may be attributed to the specific higher order steric interactions which need to be defined more precisely and incorporated into this generalized scheme. The predicted steric hindrance, equivalent to about 13.2 and 20.1 kcal/mol, in the 1,2-disubstituted ethylenes such as poly(2-methyl-2-butene) and poly(2,3-dimethyl-2-butene) is very large, as seen from the l terms of 60 and 96, respectively. This almost precludes their polymerization except for the dimers and trimers formed under very high pressures.[21] However, such polymerization (even in the liquid state) at sufficiently low temperature and high pressure is thermodynamically possible since the enthalpy of polymerization is still substantially negative, at least for the former. Assuming that the entropy of polymerization, $-\Delta S_p{}^c$(ll), is about 30 eu, the ceiling temperature for the (2-methyl-2-butene) system calculated from its $\Delta H_p{}^\circ$(ll) = 7.33 kcal/mol as given in Table II, is $-29°$ (and $-223°$ for 2,3-dimethyl-2-butene), only below which polymerization may be attempted. It is interesting to note that no steric hindrance is predicted for the 1,2 disubstitution with a single methyl group as in polyethylidene (2-butene polymer), for which the enthalpy of polymerization is large and close to ethylene. This is readily appreciated from the thermal and thermodynamic (from our preliminary heats of combustion on crude polymer) stability of polyethylidene, although it is only available through a rather unusual polymerization method.[22] The difficulty of polymerization of 2-butene through the usual free-radical or the ionic mechanisms is clearly due more to kinetic rather than to thermodynamic considerations. The enthalpies of polymerization of all the α-olefins are very close to the unsubstituted ethylene, varying only between 17.7 kcal/mol for 4,4-dimethyl-1-pentene and 20.13 kcal/mol for propylene, and are large enough to account for their ready polymerizability when a suitable mechanism became available through the Ziegler–Natta catalyst systems.

Viscoelastic and thermal properties of polymers, glass temperature, crystal structure, and most other properties depend on the chain stiffness (flexibility) which is a direct consequence of the steric hindrance in the polymer structure. In this connection, it is instructive to examine not only the enthalpy of polymerization, but also the enthalpy of formation of the polyolefin in comparison to that of linear polyethylene of the same molecular weight. The indications from both the SZ scheme and the available experimental results[14,15] are that polypropylene and all higher poly(α-olefins) are definitely about 0.5–1.5 kcal/mol more stable energetically than polyethylene, in spite of the branching; these figures suggest that the steric hindrance is small (if indeed not less than in polyethylene) for all of these isomers. Hindrance is evident in

---

(18) S. Nose, *J. Polymer Sci.*, **B2**, 1127 (1964).

(19) R. H. Wiley, G. M. Brauer, and A. R. Bennett, *ibid.*, **5**, 609 (1950).

(20) F. S. Nichols and R. G. Fowlers, *Ind. Eng. Chem.*, **42**, 292 (1950).

(21) K. E. Weale, *Quart. Rev.* (London), **16**, 267 (1962).

(22) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 272.

polyisobutylene; its enthalpy exceeds that of polyethylene by 2.36 kcal/mol, as do also the (hypothetical) α,β-disubstituted polyolefin structures 8 and 12 by about 7 and 10 kcal/mol, respectively. Tatevskii's scheme does not indicate steric hindrance in any of these branched polymers with respect to polyethylene, primarily because it lacks the necessary steric parameters capable of discriminating subtle steric differences in alkanes larger than eight carbon atoms.

Comparing the experimental $\Delta H_f°(g)$'s of the isotactic polypropylene[14,15] and the isotactic poly(1-butene)[14] with the corresponding values predicted from the SZ scheme, a steric hindrance of about 0.4 kcal for the polypropylene and about 0.8 kcal for the poly(1-butene) is observed. Since the SZ scheme does not consider steric interactions beyond 1–3 carbons, it is reasonable to assume that the enthalpies of formation calculated by this scheme would be closer to syndiotactic polymer where the higher order steric hindrance arising from a sandwiched segment of a polymer would be the least. The above energy differences for the isotactic polymers are then reconcilable. More experimental enthalpy of formation data on well-characterized polyolefins, including such totally syndiotactic polymers as polypropylene, are under way and will be useful in understanding higher order interactions which in turn should help to improve the existing bond-energy schemes for predicting properties of polymers.

Acknowledgment. The authors wish to express their sincere thanks to Dr. A. P. Kudchadker for his assistance and advice in the numerous calculations. This work was supported through the Robert A. Welch Foundation and the Texas A&M Thermodynamics Research Center.

Thermally Stable Ladder Polyquinoxalines

J. K. Stille and E. L. Mainen

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52240.

Received November 20, 1967

ABSTRACT: Five thermally stable quinoxaline polymers have been prepared by the condensation of the aromatic tetramines 1,2,4,5-tetraminobenzene and 2,3,6,7-tetraminodibenzo-*p*-dioxin with 2,5-dihydroxy-*p*-benzoquinone or the tetraketones 1,2,6,7-tetraketopyrene and 1,2,5,6-tetraketoanthracene. All of the polymers obtained were completely soluble in 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane. The polymers prepared from the condensation of 1,2,4,5-tetraminobenzene with the tetraketones 1,2,6,7-tetraketopyrene and 1,2,5,6-tetraketoanthracene had molecular weights of 7000 and 12,000, respectively. All of the polymers obtained had good thermal stability in air, although the ladder polymers were not significantly more stable than the single-strand polyquinoxalines. The thermal stability of the ladder polymers in a nitrogen atmosphere was considerably greater than that of the corresponding single-strand polymer.

The concept of new, high-performance polymers which are capable of demonstrating enhanced thermal stability has attracted much interest. One class of polymers that possess potentially useful thermal properties is the polyquinoxalines.[1-7] The thermal stability of these polymers has been attributed to their totally aromatic structure. The single-strand polyquinoxalines are yellow-brown to black in color, moderately soluble in hexamethylphosphoramide, and stable in air and nitrogen atmospheres to 500–550°.

The quinoxaline ring-forming reaction, a condensation of an *o*-diamine with a 1,2-dicarbonyl, has proven to be an efficient one for the synthesis of polymers. This reaction should be adaptable to the formation of ladder polymers and the efficiency of this reaction should ensure a perfect ladder structure. The incorporation of the quinoxaline nucleus into ladder or double-strand polymers should enhance the thermal stability of the polymer and allow an investigation of the ladder polymer concept as applied to heterocyclic polymers.

Discussion

In order to utilize the quinoxaline-forming reaction for the synthesis of ladder polymers, amine monomers containing two sets of aromatic *o*-diamine functions doubly joined and ketone monomers containing two sets of 1,2-dicarbonyls doubly linked are required. Ideally, the attachment of the sets of functions is such that the resulting polymer will be totally aromatic. When 2,5-dihydroxy-*p*-benzoquinones and aromatic tetramines were polymerized, dihydroquinoxaline polymers were obtained.

The polymerization of 2,5-dihydroxy-*p*-benzoquinone (I) with 1,2,4,5-tetraminobenzene (II) or its hydrochloride salt in hexamethylphosphoramide or 116% polyphosphoric acid gave VIII.[8] The degree of polym-

---

(1) J. K. Stille and J. R. Williamson, *J. Polymer Sci.*, **B2**, 209 (1964).

(2) J. K. Stille and J. R. Williamson, *ibid.*, **A2**, 3867 (1964).

(3) J. K. Stille, J. R. Williamson, and F. E. Arnold, *ibid.*, **A3**, 1013 (1965).

(4) J. K. Stille and F. E. Arnold, *ibid.*, **A4**, 551 (1966).

(5) G. DeGaudemaris and B. Sillion, *ibid.*, **B2**, 203 (1964).

(6) G. DeGaudermaris, B. Sillion, and J. Preve, *Bull. Soc. Chim. France*, 1793 (1964).

(7) P. M. Hergenrother and H. H. Levine, *J. Polymer Sci.*, **A1**, **5**, 1453 (1967).

(8) The names of the polymers appear in the Experimental Section. We wish to thank the Chemical Abstracts Service for suggesting these names.