

Influence of the Structural Order on Thermodynamic Properties for Three Different Polyethylenes

INTRODUCTION

The thermodynamic properties of polyethylene are of great importance for industrial use, especially at those pressures and temperatures which are maintained in the commercial production of polyethylene. During classical high pressure polymerization of ethylene by radical mechanism, various structurally different, mostly branched molecules could be obtained, which differ in chain length and degree of branching. It was reported recently^{1,2} that linear low density polyethylene could be obtained at high pressure, as well. From these points of view, it is necessary to provide accurate thermodynamic data of polyethylenes, having various molecular structures, for the design and operation of high pressure plants. This is especially important for the reacting and the separating sections of the process.

In spite of the difficulties in obtaining the experimental volumetric data at high pressure and temperature, or establishing the numerical parameters, necessary in the procedures for their computation, both kinds of data became more readily available in the last period.³⁻¹¹ Concerning the other basic thermodynamic properties (internal energy, enthalpy, entropy), only scarce calculated data exist.^{3,8,11,13} It should be noted that the existing data are often limited with respect to the pressure and temperature, and sometimes also with respect to their accuracy. The choice of the representative polyethylene sample must be done carefully, if the obtained results are to be properly used and compared with the other available data. Zoller¹² used three LDPE samples, all of which were branched. Olabisi and Simha¹¹ reported experimental p - v - T data for three different polyethylenes, as well as the way for their analytical representation. Only few data, however, considered the influence of branching on the thermodynamic properties of polyethylene.¹⁴⁻¹⁷

In this work, specific volume, internal energy, enthalpy, and entropy of three structurally different polyethylenes are calculated as functions of temperature and pressure. The ranges of temperature and pressure are so chosen to correspond to the industrial conditions during polymerization of ethylene at high pressures.

RESULTS AND DISCUSSION

Thermodynamic properties of three different polyethylenes, i.e., linear (LPE), branched (BPE), and ultrahigh molecular weight linear polyethylene (HMLPE), are calculated for the temperature range 400–500 K and pressures up to 200 MPa. Two of them (LPE and BPE) represent standard polyethylene samples (SRM 1475 and SRM 1476). The volumetric properties were calculated using Tait equation of state

$$1 - v/v_0 = C \ln(1 + P/B) \quad (1)$$

where v_0 and v represent specific volumes at atmospheric pressure and pressure P , respectively, and $C = 0.0894$ is an empirical constant for the considered polymers.¹⁸ It was shown^{10,19,20} that constant B could be expressed by

$$B = B_0 \exp(-B_1 \cdot T) \quad (2)$$

whereby the numerical values for constants B_0 and B_1 are given in Table I. It was concluded by Olabisi and Simha¹¹ that v_0 is adequately represented by

$$v_0 = V \exp(\alpha_1 T) \quad (3)$$

TABLE I
Numerical Values of the Constants in eqs. (2) and (3)¹¹

	B_0 (MPa)	B_1 (1/K) $\times 10^3$	α_1 (1/K) $\times 10^4$	V (m ³ /kg) $\times 10^{-3}$
LPE	179.04	4.661	7.80	0.9172
BPE	179.45	4.699	7.34	0.9399
HMLPE	170.53	4.292	8.50	0.8992

The values of V and α_1 for three investigated polyethylenes are presented in Table I.

Figure 1 shows the comparison of the volumetric properties for BPE calculated in this work with the published data of the other authors. The present results show good agreement with the other published experimental and calculated values, except with those of Matsuoka.⁴ Similar disagreement about experimental data of Matsuoka was also noted by Foster et al.⁷ The comparative volumetric properties, for three investigated polyethylenes, are presented in Figure 2.

To derive other thermodynamic properties (internal energy, enthalpy, and entropy) the approach of Maloney and Prausnitz¹⁰ was used. The rigorous thermodynamic equation can be applied for the purpose of all calculations performed in this work. The change of entropy with temperature, at atmospheric pressure

$$dS = (C_p/T) dT \quad (4)$$

incorporates the heat capacity in the form²¹ $C_p = 0.3743 + 5.58 \times 10^{-4}T$. Integration of Maxwell equation $(\partial S/\partial v)_T = (\partial P/\partial T)_v$, and $dU = TdS - pdv$, using the Tait equation of state (1), results in the forms

$$S_2 - S_1 = (d \ln B/dT) [B(v_0 - v) - Cv_0P] + (d \ln v_0/dT) [B(v_0 - v) - P(v + Cv_0)], T = \text{const} \quad (5)$$

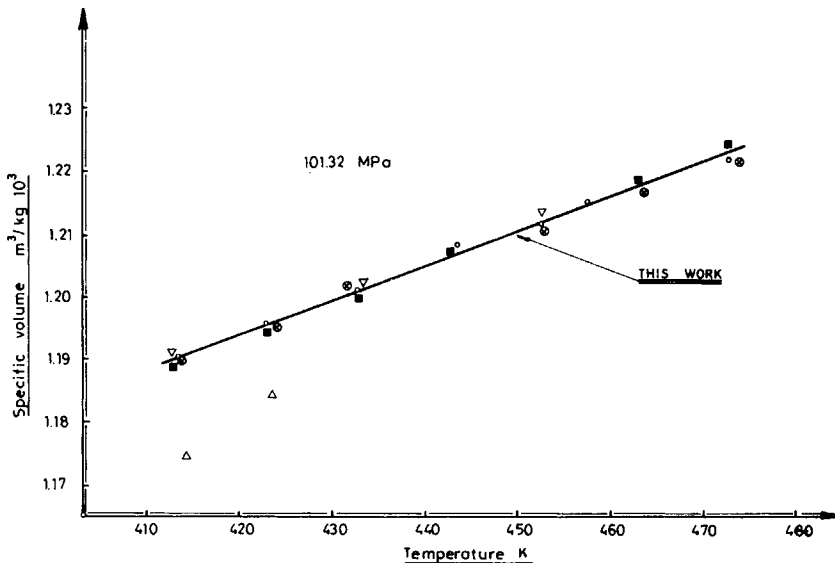


Fig. 1. Comparison of the volumetric properties for BPE: (▽) Parks and Richards³; (○) Olabisi and Simha¹¹; (△) Matsuoka⁴; (⊗) Zoller¹²; (■) this work.

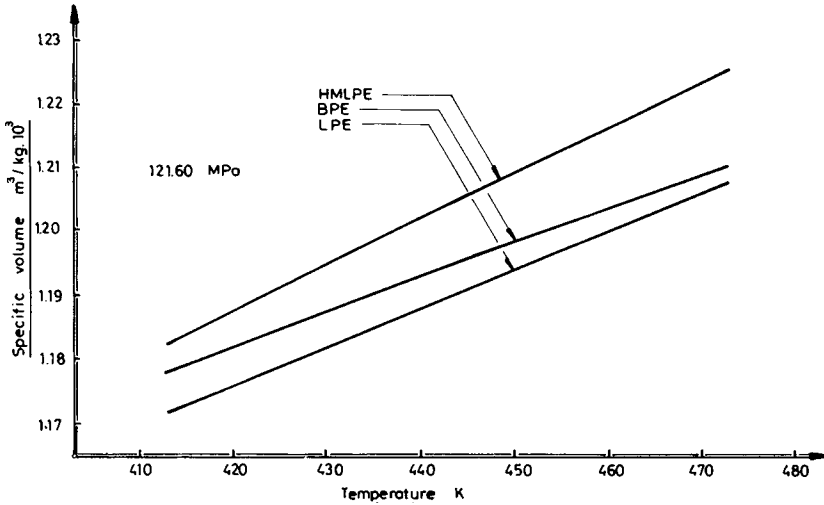


Fig. 2. Calculated volumetric properties for three polyethylenes.

$$U_2 - U_1 = T(S_2 - S_1) + v_0 CP - B(v_0 - v), T = \text{const} \quad (6)$$

Enthalpy is determined by definition

$$H = U + pv \quad (7)$$

The detailed procedure for these calculations was given elsewhere.^{10,13} In order to obtain positive values of internal energy and enthalpy, the reference values of 418.6 kJ/kg at 373 K and 1.01325 kPa, were arbitrarily chosen, as proposed by Maloney and Prausnitz.^{10,13} For entropy, the reference value of 4.186 kJ/kg · K, for the same temperature and pressure, was adopted.

From Figures 2-5 it can be concluded that thermodynamic properties of polyethylene are influenced by different structural order. This fact should not be neglected if precise and

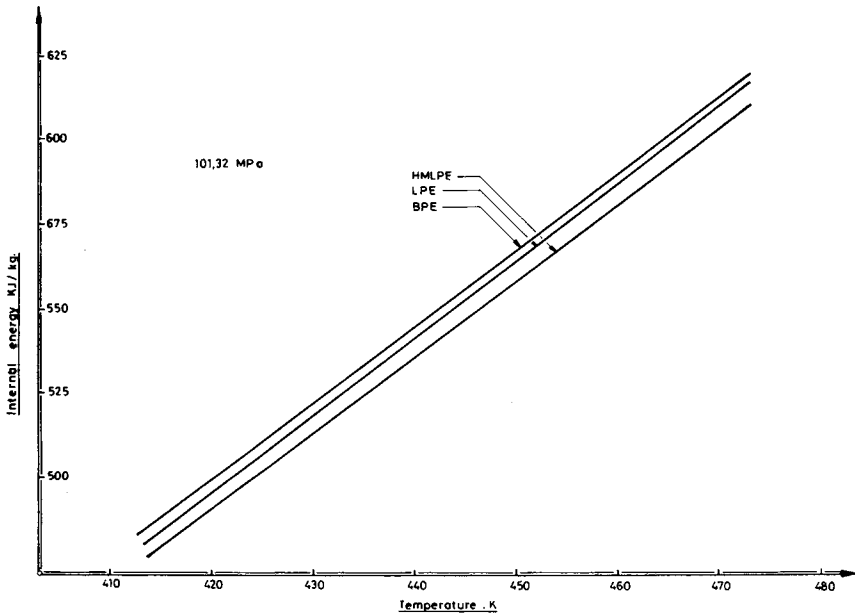


Fig. 3. Calculated internal energies for three polyethylenes.

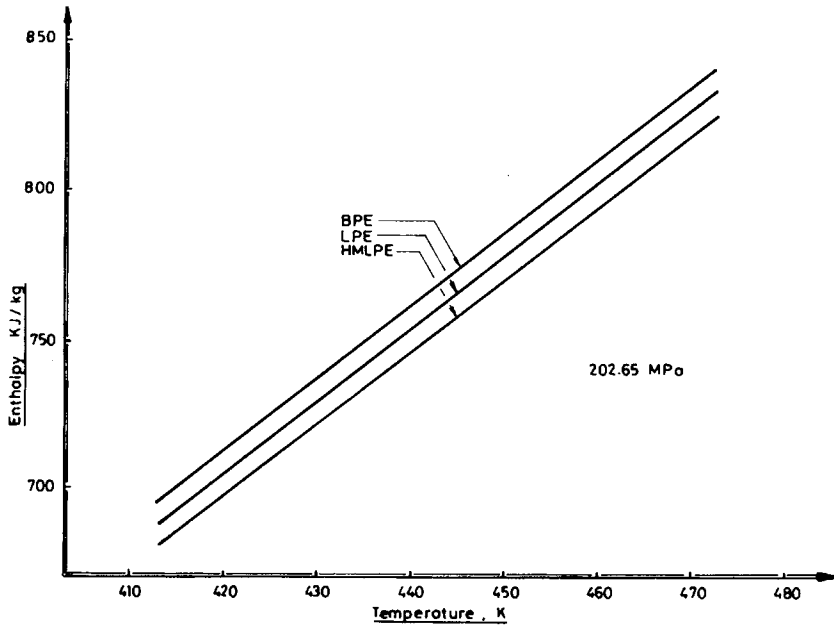


Fig. 4. Calculated enthalpies for three polyethylenes.

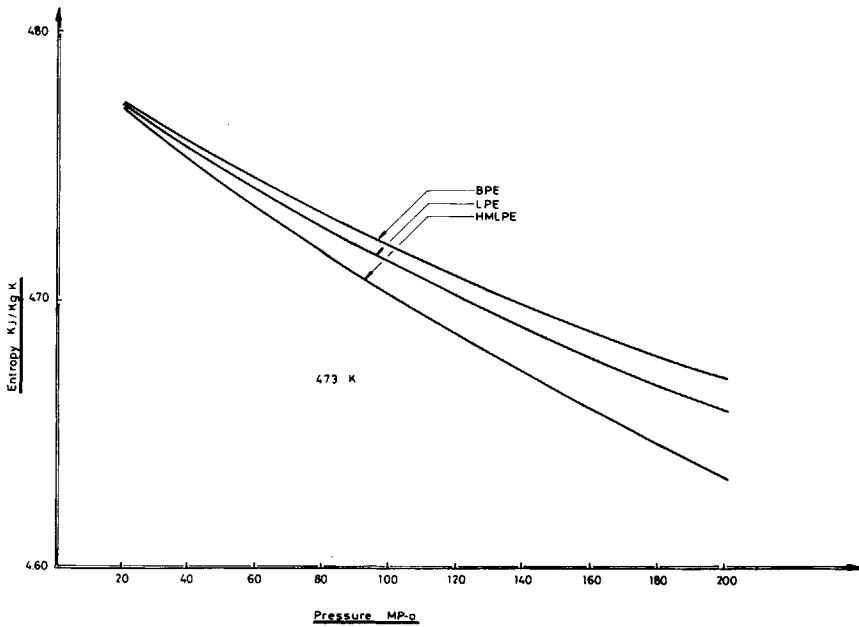


Fig. 5. Calculated entropies for three polyethylenes.

theoretically correct treatment is required. Such statement is in accordance with other authors,^{14,15} who investigated the effect of chain branching on various thermodynamic properties of polyethylene, although the opposite opinions could be also found (e.g., Chung⁶). Since it is well known that minor structural differences have significant influence on all physicochemical properties of low density polyethylene for end use, it is quite logical that structurally different polyethylenes have influence on their thermodynamic properties as well. The results obtained may be used to establish the influence of structural order on basic thermodynamic properties of polyethylene in the molten state and for engineering design of the commercial high pressure polyethylene units.

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