COR-eos and BH-eos Parameters for Polymer Melts with the Error in the All-Variables Method

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SYNOPSIS

All the data for more than 100 polymer melts in a PVT data base were used to determine best-fit characteristic parameters for two different theoretical equations-of-state (eos): the chain-of-rotators (COR) and the Bruce Hartmann (BH) eos. Fitting was performed by applying an error in all-variables algorithm that was recently developed by Hartmann et al. Despite their very different theoretical basis, both equations-of-state led to close descriptions of the PVT surface with comparable average deviations. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Theoretical equations-of-state require superposition of a theoretical and an experimental PVT surface, which is the first step for all applications of such equations-of-state within any thermodynamic model. The determination of their characteristic (or reducing) parameters is a difficult task even today. Experimental PVT data for more than 100 polymers in the melt state[1-48] have been collected in a data bank by Wohlfarth.[49] This data bank provides about 10,000 PVT triples and may be used to test theoretical equations-of-state and to determine their characteristic parameters as well.

Recently, Hartmann et al.[50] developed an algorithm with an error in an all-PVT-variables method and tested it with 11 polymers for the Simha/Somcynsky (SS)[51] and the Bruce Hartmann (BH)[52,53] equations-of-state.

Wohlfarth[54] applied the chain-of-rotators (COR) equation-of-state (eos)[55] to most of the polymers in his data bank and determined their characteristic parameters, but using a conventional simultaneous fit procedure where all experimental uncertainty is assumed to belong to the volume data only. The aim of this paper was to apply the error in the all-variables method also to the COR-eos and to extend the investigations with the BH-eos to all suitable PVT

data sets from the data bank. This is followed by a discussion of the findings.

THE EQUATIONS-OF-STATE

Chain-of-Rotators Equation-of-State

The COR-eos was developed by Chao and his group[55] for an application to phase equilibria in hydrocarbon mixtures. It results from a combination of the hard-core equations of Carnahan/Starling[56] and Boublik/Nezbeda[57] for the separate consideration of rotational degrees of freedom within the model. An attractive term based on thermodynamic perturbation theory is added. The final result reads[55]

$$\frac{PV}{RT} = 1 + \frac{4y^2 - 2y}{(y-1)^3}$$
$$+ \frac{c}{2}(\alpha - 1)\frac{3y^2 + 3\alpha y - (\alpha + 1)}{(y-1)^3}$$
$$+ \frac{U}{RT^*}\sum_m \sum_n \frac{m \cdot A_{nm}}{\tilde{T}^n \cdot \tilde{V}^m} \quad (1)$$

or

$$Z = \frac{PV}{RT} = Z_{trans} + cz_{rot} + Z_{attr} \quad (2)$$

where P is pressure; V, molar volume; T, absolute

temperature; R, universal gas constant; T^*, characteristic temperature; $\tilde{V} = V/V_0$, and $y = \tilde{V}/\tau$ with V_0 the closest packed volume; $\tau = \pi \sqrt{2}/6 = 0.7405$; $\alpha = 1.078$, dumbbell constant (ethane); c, number of rotational degrees of freedom (per mole of chains); U, characteristic energy; and $\tilde{T} = T/T^*$, reduced temperature:

$$\frac{U}{RT^*} = 1 + \frac{c}{2} \cdot B(\tilde{T}),$$

$$B(\tilde{T}) = \left(B_0 + \frac{B_1}{\tilde{T}} + B_2 \cdot \tilde{T} \right) \quad (3)$$

Chien et al.[55] adjusted the empirical coefficients A_{nm} and B_i to the PVT data, internal energies, and vapor pressure data of methane, ethane, and propane. These coefficients are considered to be "universal" constants for all our calculations in this work. Finally, three parameters remain in the COR-eos, i.e., V_0, c, and T^*, which must be fitted to experimental PVT data (which is the special aim of this work). Originally, the COR-eos was not thought to be applicable to polymer melts. Its main purpose was the calculation of phase equilibria in solvent mixtures. Regener et al.[58,59] also proved the COR-eos to be useful for phase equilibrium calculations in polymer solutions. Wohlfarth and co-workers applied the COR-eos to high-pressure phase equilibria in monomer/polymer mixtures.[60] As all these calculations are rather sensitive with respect to the characteristic parameters of the pure components, the error in the all-variables-fit procedure now provides more accurate parameters for this task.

Bruce Hartmann Equation-of-State

The BH-eos was developed by Hartmann and Haque.[52,53] It results from a skillful combination of a relationship found by Pastine and Warfield[61] and the Simha/Somcynsky theory.[51] The BH-eos reads

$$\tilde{P}\tilde{V}^5 = \tilde{T}^{3/2} - \ln \tilde{V} \quad (4)$$

with

$$\tilde{P} = P/P_0, \quad \tilde{T} = T/T_0, \quad \text{and} \quad \tilde{V} = V/V_0,$$

This eos is in the form of a corresponding states relationship, i.e., all polymers follow the same eos in terms of reduced variables. The three scaling parameters have again to be fitted to experimental PVT data as was done in paper[50] and is continued here.

Hartmann could show that this surprisingly simple eos is good for polymer liquids and glasses. Furthermore, it does not have too many problems concerned with compressibility, which occur, e.g., with the application of the Flory–Orwoll–Vrij-eos[62] if this eos is used to calculate the PVT surface with the characteristic parameters obtained from normal pressure data only.

Error in All-Variables Algorithm[50]

Both eos under consideration are pressure-explicit equations and may be written as

$$P = P(V, T, c, T^*, V_0) \quad \text{COR-eos} \quad (5a)$$

$$P = P(V, T, P_0, V_0, T_0) \quad \text{BH-eos} \quad (5b)$$

Let there be given N experimental data points (P_i, V_i, T_i), $i = 1, \ldots, N$, with given standard deviations $\sigma_i(P)$, $\sigma_i(V)$, and $\sigma_i(T)$ for the corresponding measurement errors. The characteristic parameters are determined by minimizing a function $SSQ(c, T^*, V_0)$ or $SSQ(P_0, V_0, T_0)$, respectively, which is defined as follows: A set of the characteristic parameters may be given (as an initial guess or its stepwise improved value).

For each $i = 1, \ldots, N$, set

$$S_i^2(P, V, T)$$
$$= \frac{(P - P_i)^2}{\sigma_i(P)^2} + \frac{(V - V_i)^2}{\sigma_i(V)^2} + \frac{(T - T_i)^2}{\sigma_i(T)^2} \quad (6)$$

and find the $[P(i), V(i), T(i)]$ triple that satisfies the considered eq. (5) and minimizes S_i^2. As P is to be substituted by eq. (5), this is equivalent to finding the $[V(i), T(i)]$ pair that minimizes eq. (6). Let D_i^2 denote the value $S_i^2[V(i), T(i)]$ and note that D_i^2 is, in fact, a function of the characteristic parameters. The function SSQ is defined as

$$SSQ(c, T^*, V_0) = \sum_{i=1}^{N} D_i^2(c, T^*, V_0) \quad (7a)$$

or

$$SSQ(P_0, V_0, T_0) = \sum_{i=1}^{N} D_i^2(P_0, T_0, V_0) \quad (7b)$$

Finding the parameter set that minimizes SSQ has to be done by a nonlinear fitting program. For this, one needs, however, to supply a routine for evalu-

Table I   Characteristic Parameters of COR-eos for Molten Polymers and Copolymers Estimated by the Error-in-All-Variables Method

No.	Polymer	$V_{0,spec}$ (cm^3/g)	C_{spec} (mol/g)	T^* (K)	$T \rightarrow$ Range $\leftarrow P$ (K)	(MPa)	SSQ/N	Ref.
1	HDPE	0.77817	0.15906	429.515	438–473	0–200	0.01	2
2	HDPE(high)	0.77382	0.19144	410.929	420–472	0–200	0.02	2
3	HDPE	0.78279	0.12960	427.635	423–580	1–770	0.96	4
4	HDPE	0.77733	0.16053	428.236	415–473	0–200	0.01	16
5	HDPE	0.81394	0.10156	496.093	413–476	0–180	9.42	41
6	HDPE	0.81345	0.16590	471.277	453–523	0–62	18.28	42
7	HDPE	0.80384	0.12156	472.616	433–493	0–3	0.18	23
8	HDPE	0.79283	0.15058	448.272	413–543	0–200	25.60	35, 36
9	LDPE	0.80010	0.12060	472.097	433–493	0–3	0.04	23
10	LDPE	0.79260	0.13729	448.541	408–471	0–100	0.40	2
11	LDPE	0.78971	0.14201	452.826	393–503	0–200	6.53	22
12	LDPE	0.79373	0.13860	461.120	393–503	0–200	7.04	22
13	LDPE	0.79097	0.14130	456.492	393–503	0–200	8.21	22
14	LDPE	0.79215	0.13840	450.188	394–448	0–180	9.19	41
15	LDPE-wax	0.76348	0.10705	399.250	393–473	0–200	75.00	29
16	LDPE-wax	0.76838	0.10584	409.797	393–473	0–200	95.00	29
17	LDPE-wax	0.79266	0.12003	435.337	398–498	0–200	6.78	28
18	LDPE-wax	0.79245	0.12829	445.424	373–473	10–80	0.09	46
19	PIB	0.73131	0.12932	456.522	323–383	0–100	0.96	5
20	PP(iso)	0.81029	0.10483	484.543	473–553	0–200	3.95	21
21	PP(iso)	0.81548	0.08219	504.633	443–575	1–441	1.97	8
22	PP(iso)	0.84064	0.10279	526.638	453–523	0–180	30.24	41
23	PP(iso)	0.82725	0.11572	499.880	453–523	0–62	185.90	44
24	PB1(iso)	0.79213	0.11330	471.845	463–503	0–150	1.47	21
25	PB1(iso)	0.71623	0.22307	378.582	483	10–478	0.02	7
26	cis-1,4-PBD	0.71436	0.18416	367.410	277–317	0–200	9.61	24
27	cis-1,4-PBD	0.75322	0.10853	468.555	343–373	0–100	0.06	18
28	P4MP1	0.82439	0.09856	485.253	513–592	0–160	4.95	9
29	NR	0.71024	0.17495	390.513	273–298	0–50	0.41	26
30	NRvulc.	0.71706	0.17303	394.607	273–298	0–50	0.36	26
31	PS	0.64368	0.12081	498.053	373–493	0–200	0.10	14
32	PS	0.64627	0.09987	525.554	388–468	0–160	2.97	10
33	PS(785)	0.66431	0.11282	497.190	354–525	0–200	0.03	39
34	PS(1840)	0.65335	0.12640	492.583	393–523	0–200	0.04	39
35	PS(3580)	0.65581	0.11637	515.773	403–523	0–200	0.02	39
36	PS(8500)	0.65214	0.11878	511.049	403–523	0–200	0.02	39
37	PS(17000)	0.65013	0.11767	514.320	403–503	0–200	0.01	39
38	PS(32500)	0.64844	0.11863	511.226	403–503	0–200	0.01	39
39	PS(104000)	0.64971	0.11111	523.500	403–523	0–200	0.03	39
40	PS(109800)	0.64422	0.11685	510.468	413–503	0–200	0.01	39
41	PS(239800)	0.64854	0.11172	529.021	433–577	0–200	0.04	39
42	PS(577000)	0.65297	0.11768	509.957	413–523	0–200	0.01	39
43	PS(815000)	0.64816	0.11234	521.810	413–523	0–200	0.02	39
44	PoMS	0.65902	0.08854	591.385	407–471	0–140	0.02	10
45	PVAc	0.54993	0.15304	398.532	308–368	0–80	5.60	1
46	PVAc	0.55776	0.16566	406.028	373–473	10–80	0.08	46
47	PMMA	0.56318	0.12024	495.962	397–432	0–160	0.01	2
48	PMMA(iso)	0.54989	0.13997	471.586	332–447	0–200	0.14	3
49	PnBMA	0.63059	0.13931	431.083	307–470	0–200	0.10	2
50	PnBMA	0.63019	0.14007	430.089	320–472	0–200	0.11	16
51	PCHMA	0.60689	0.11127	494.661	383–473	0–200	0.04	2

Table I *(Continued)*

No.	Polymer	$V_{0,spec}$ (cm³/g)	C_{spec} (mol/g)	T^* (K)	$T \rightarrow$ Range $\leftarrow P$ (K)	(MPa)	SSQ/N	Ref.
52	PCPMA	0.59310	0.12701	465.717	353–483	0.1	0.20	17
53	NY 66	0.61502	0.17571	517.100	533–573	0–100	0.09	34
54	PTFE	0.31527	0.05220	407.375	603–645	0–40	11.07	11
55	PPFE(typ Y)	0.33233	0.05792	346.160	298–373	0–40	0.02	38
56	PPFE(typ Z)	0.33541	0.06932	331.883	298–373	0–40	0.01	38
57	PPFE(S-20)	0.33113	0.07671	306.910	273–333	0–180	4.90	45
58	PPFE(S-65)	0.33539	0.06548	328.533	293–333	0–170	4.80	45
59	PPES	0.49184	0.10315	610.494	513–623	0–200	0.01	30
60	PSF	0.53751	0.12624	553.221	533–613	0–200	0.72	12
61	PPE	0.58344	0.13474	451.674	373–593	0–200	0.08	14
62	PET	0.50864	0.12969	525.796	533–613	0–200	0.79	15
63	PBT	0.53586	0.14464	494.074	508–578	0–200	0.10	48
64	PHENOXY	0.57635	0.15330	499.378	373–573	0–180	6.27	13
65	PARYL	0.54832	0.11590	545.780	453–573	0–180	6.63	13
66	PEEK	0.52710	0.11516	559.037	618–678	0–200	0.43	40
67	PC	0.55416	0.12627	514.551	423–613	0–180	5.56	13
68	POM	0.52018	0.14158	473.307	458–500	0–200	0.44	33
69	PEO	0.59629	0.15166	429.968	353–393	0–40	8.10	31
70	PEO	0.59127	0.18986	416.913	353–443	0.1	0.29	47
71	PEO	0.59080	0.16922	413.361	333–393	0–40	0.01	46
72	PEO	0.60696	0.15038	439.482	373–473	10–80	0.07	46
73	PEO	0.59467	0.16276	431.074	353–400	0–200	0.02	30
74	PDMS(8800)	0.64700	0.11722	330.362	293–353	0–200	14.74	32
75	PDMS(30500)	0.64117	0.13011	324.647	293–353	0–200	24.58	32
76	PDMS(162)	0.76851	0.16681	267.642	298–343	0–90	0.87	6
77	PDMS(594)	0.67680	0.12721	306.280	298–343	0–90	1.03	6
78	PDMS(958)	0.67117	0.12330	320.573	298–343	0–90	1.23	6
79	PDMS(1540)	0.65819	0.12076	326.514	298–343	0–90	1.82	6
80	PDMS(4170)	0.64825	0.12167	329.873	298–343	0–90	2.50	6
81	PDMS(6560)	0.64776	0.11570	335.240	298–343	0–90	2.17	6
82	PDMS(7860)	0.64781	0.11578	334.986	298–343	0–90	2.22	6
83	PEtS(626)	0.66498	0.13249	384.130	313–373	0–200	5.46	27
84	PEtS(1617)	0.63249	0.12441	395.410	313–373	0–200	8.83	27
85	PEtS-2	0.68533	0.15508	348.559	313–373	0–200	4.29	25
86	OCS(XC-2-1)	0.64634	0.09929	424.189	292–574	0–50	173.00	37
87	OCS(XC-2-1 BB)	0.63820	0.09277	423.160	292–574	0–50	286.00	37
88	OFS(FC-T-5)	0.58651	0.10766	400.144	292–574	0–50	199.00	37
89	EPR	0.82630	0.10623	520.042	413–523	0–62	16.45	41
90	BS(25)	0.72088	0.09786	443.654	343–373	0–100	0.07	18
91	BS(48)	0.69403	0.11088	457.073	343–373	0–100	0.06	18
92	BS(70)	0.67436	0.10719	498.446	343–373	0–100	0.01	18
93	SBS(25.4)	0.71832	0.11596	455.706	343–373	0–100	0.01	18
94	SBS(30)	0.71882	0.11416	459.150	343–373	0–100	0.05	18
95	EVA18	0.76916	0.13541	457.980	403–507	0–180	6.48	20
96	EVA25	0.75003	0.13065	452.220	403–507	0–180	6.87	20
97	EVA28	0.74584	0.13856	450.806	403–517	0–180	6.45	20
98	EVA40	0.71239	0.13135	454.316	412–508	0–100	3.76	20
99	EVA22	0.75502	0.11439	502.925	398–498	0–200	0.19	19
100	EVA32	0.75132	0.10465	522.176	398–498	0–200	0.16	19
101	EVA42	0.71725	0.11935	500.281	398–498	0–200	0.17	19
102	EVA09	0.75489	0.17768	408.604	373–473	10–80	0.08	46
103	EVA20	0.73776	0.08817	461.013	353–422	5–40	0.04	46

Table I   *(Continued)*

No.	Polymer	$V_{0,spec}$ (cm^3/g)	C_{spec} (mol/g)	T^* (K)	$T \rightarrow$ Range $\leftarrow P$ (K)	(MPa)	SSQ/N	Ref.
104	EVA28	0.72563	0.13659	427.926	373–437	10–80	0.14	43
105	EVA-wax	0.73090	0.13683	436.556	398–443	58–392	0.13	28

Abbreviations: in ( ), type or tacticity or number-average molecular weight or mass percent of comonomer contents; HDPE, high-density polyethylene (high, high molecular weight sample); LDPE, low-density polyethylene; PIB, polyisobutylene; PP1 polypropylene; PB1, poly(1-butene); cis-1,4-PBD, cis-1,4-polybutadiene; P4MP1, poly(4-methyl-1-pentene); NR, natural rubber; PS, polystyrene; PoMS, poly(ortho-methylstyrene); PVAc, poly(vinyl acetate); PnBMA, poly(n-butyl methacrylate); PMMA, poly(methyl methacrylate); PCHMA, poly(cyclohexyl methacrylate); PCPMA, poly(cyclopentyl methacrylate); NY 66, nylon 66; PTFE, polytetrafluoroethylene; PPFE, poly-perfluoroether; PPES, poly(p-phenylene ether sulfone); PSF, polysulfone; PPE, poly(2,6-dimethyl-1,4-phenylene ether); PET, poly(ethylene terephthalate); PBT, poly(butylene terephthalate); PHENOXY, poly(oxy-2-hydroxytrimethyleneoxy-1,4-phenylene-iso-propylidene-1,4-phenylene); PARYL, polyester from bisphenol-A and 50/50 iso- and terephthalic acid; PC, bisphenol-A polycarbonate; POM, polyoxymethylene; PEO, poly(ethylene oxide); PDMS, polydimethylsiloxane; PEtS, polyethylsiloxane; OCS, oligoorganochlo-rosiloxane; OFS, oligoorganofluorosiloxane; EPR, ethylene–propylene rubber; BS(x), butadiene–styrene copolymer (Ma % styrene); SBS(x), polystyrene-*block*-polybutadiene-*block*-polystyrene triblockcopolymer (Ma % styrene); EVA, ethylene–vinyl acetate copolymer (Ma % vinyl acetate).

ating each "residual" D_i, i.e., a subroutine that minimizes eq. (6) for each experimental point and a given parameter set. This has to be done by solving the pair of eqs. (8) (with a nonlinear equation solving procedure):

$$\frac{\partial S_i^2 [V(i), T(i)]}{\sigma V} = 0$$

$$\text{and} \quad \frac{\partial S_i^2 [V(i), T(i)]}{\sigma T} = 0 \qquad (8)$$

More details of the procedure are given in Ref. 50.

RESULTS AND DISCUSSION

COR-eos and BH-eos parameters were determined for more than 100 polymers (or copolymers) in the melt state, where PVT data were available over certain temperature and pressure ranges. Generally, fitting to one single isotherm or isobar is difficult and seldom leads to satisfying results (there are three examples, nos. 25, 52, and 70, in Table I, where reasonable parameters could be obtained for the COR-eos but no solution was found with the BH-eos, Table II). Thus, a number of data sets from the data bank were not used as they do not contain sufficient data.

Furthermore, no parameter fitting was made to data sets with thermal coefficients at normal pressure only. In some cases (polymers with nos. 11–13, 20, 24, 53, 62, 64–68, 76–82), the characteristic parameters could be fitted only to PVT data that had to be recalculated from Tait equation parameters

(e.g., [21, 22]). Of course, experimental scattering is smoothed out in these data. Nevertheless, reasonable characteristic parameters can be determined also in such cases.

The standard deviations were chosen mainly by following Zoller* and his extensive experience about what are reasonable errors in PVT measurements for polymer melts. $\sigma_i(P) = 0.002$ MPa was used for all atmospheric pressure data points for all polymers. At higher pressures, $\sigma_i(P) = 0.005P_i$ was generally used. $\sigma_i(T) = 0.1$ K was applied throughout all calculations, as this is the most reasonable value even when authors claim more precise thermostating. As standard deviations for V_i, values of $\sigma(V_i) = 0.004V_i$ (polymers with nos. 1–3, 10, 21, 25, 27, 31, 33–43, 46–52, 55, 56, 59, 61, 63, 73, 90–94, 99–104) and $\sigma(V_i) = 0.0004$ V_i (in all other cases) were applied. This looks somewhat arbitrary but higher claimed precision seems to be unrealistic. Zoller* is known for precise measurements and states $0.004V_i$ for his PVT apparatus; other authors claim $0.0004V_i$ for their results. Thus, both values reflect the usual range for PVT data of polymer melts.

All parameters for both COR- and BH-eos are summarized in Tables I and II, together with the temperature and pressure ranges of the experimental data and the resulting SSQ/N. All parameters are listed with five or six digits (one or two digits more than one would expect to being significant in comparison with the accuracy of the experimental data), which have been proven to be necessary to calculate

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* Gnomix Inc., Boulder, Colorado, produces the best available PVT machine. For many results, see papers by Zoller in the Reference section.

Table II   Characteristic Parameters of BH-eos for Molten Polymers and Copolymers Estimated by the Error-in-All-Variables Method

No.	Polymer	$V_{0,spec}$ (cm³/g)	P_0 (MPa)	T_0 (K)	$T \rightarrow$ Range $\leftarrow P$ K	MPa	SSQ/N	Ref.
1	HDPE	1.03444	2827.99	1197.12	438–473	0–200	0.02	2
2	HDPE(high)	1.02301	3234.80	1125.66	420–472	0–200	0.02	2
3	HDPE	1.15772	2493.15	1845.60	423–580	1–770	1.09	4
4	HDPE	1.03492	2822.88	1198.89	415–473	0–200	0.02	16
5	HDPE	1.09753	2147.65	1468.70	413–476	0–180	12.43	41
6	HDPE	1.08094	3119.75	1312.12	453–523	0–62	17.70	42
7	HDPE	1.06209	2352.62	1291.77	433–493	0–3	0.18	23
8	HDPE	1.06383	2593.36	1280.34	413–543	0–200	26.50	35, 36
9	LDPE	1.05711	2340.50	1290.13	433–493	0–3	0.04	23
10	LDPE	1.06272	2550.65	1290.78	408–471	0–100	0.45	2
11	LDPE	1.07109	2536.74	1354.25	393–503	0–200	6.13	22
12	LDPE	1.07826	2530.98	1391.21	393–503	0–200	6.17	22
13	LDPE	1.07374	2546.82	1371.23	393–503	0–200	4.42	22
14	LDPE	1.06528	2629.73	1314.30	394–448	0–180	6.46	41
15	LDPE-wax	1.02987	1827.07	1087.21	393–473	0–200	28.00	29
16	LDPE-wax	1.04263	1702.48	1205.72	393–473	0–200	38.50	29
17	LDPE-wax	1.05602	2194.98	1202.27	398–498	0–200	6.78	28
18	LDPE-wax	1.06225	2338.80	1275.41	373–473	10–80	0.13	46
19	PIB	0.98943	2994.65	1390.66	323–383	0–100	0.93	5
20	PP(iso)	1.10009	1865.89	1438.01	473–553	0–200	3.12	21
21	PP(iso)	1.23831	1141.27	3268.92	443–575	1–441	1.97	8
22	PP(iso)	1.12204	2168.73	1491.19	453–523	0–180	37.70	41
23	PP(iso)	1.10008	2301.55	1395.10	453–523	0–62	184.6	44
24	PB1(iso)	1.07902	2024.07	1425.23	463–503	0–150	1.94	21
25	PB1(iso)	Did not find a solution			483	10–478		7
26	cis-1,4-PBD	0.97939	3455.80	1161.59	277–317	0–200	0.39	24
27	cis-1,4-PBD	1.03177	2500.95	1543.32	343–373	0–100	0.05	18
28	P4MP1	1.11113	1698.39	1393.99	513–592	0–160	8.17	9
29	NR	0.96084	3705.37	1157.15	273–298	0–50	0.18	26
30	NRvulc.	0.97080	3717.78	1175.20	273–298	0–50	0.09	26
31	PS	0.87854	3072.61	1559.89	373–493	0–200	0.07	14
32	PS	0.87238	2981.05	1574.36	388–468	0–160	2.37	10
33	PS(785)	0.88915	3049.47	1355.97	354–525	0–200	0.16	39
34	PS(1840)	0.87526	3343.16	1391.15	393–523	0–200	0.08	39
35	PS(3580)	0.87443	3175.54	1444.23	403–523	0–200	0.06	39
36	PS(8500)	0.87462	3243.10	1462.37	403–523	0–200	0.04	39
37	PS(17000)	0.86870	3222.54	1468.91	403–503	0–200	0.03	39
38	PS(32500)	0.86877	3223.20	1477.45	403–503	0–200	0.04	39
39	PS(104000)	0.86946	3082.93	1506.93	403–523	0–200	0.10	39
40	PS(109800)	0.86099	3161.72	1461.41	413–503	0–200	0.04	39
41	PS(239800)	0.86470	3062.01	1496.62	433–577	0–200	0.12	39
42	PS(577000)	0.87184	3088.26	1453.08	413–523	0–200	0.05	39
43	PS(815000)	0.86865	3082.19	1510.40	413–523	0–200	0.06	39
44	PoMS	0.88579	3120.07	1579.66	407–471	0–140	2.12	10
45	PVAc	0.73651	3827.06	1148.91	308–368	0–80	1.28	1
46	PVAc	0.74108	3827.16	1128.67	373–473	10–80	0.11	46
47	PMMA	0.75652	3846.73	1452.36	397–432	0–160	0.01	2
48	PMMA(iso)	0.74191	4179.45	1403.45	332–447	0–200	0.21	3
49	PnBMA	0.85140	3161.94	1276.78	307–470	0–200	0.24	2
50	PnBMA	0.85386	3117.50	1291.06	320–472	0–200	0.24	16
51	PCHMA	0.81719	3162.92	1457.58	383–473	0–200	0.10	2
52	PCPMA	Did not find a solution			353–483	0.1		17
53	NY 66	0.81443	4678.24	1423.01	533–573	0–100	0.07	34

Table II (*Continued*)

No.	Polymer	$V_{0,spec}$ (cm^3/g)	P_0 (MPa)	T_0 (K)	$T \rightarrow$ Range $\leftarrow P$		SSQ/N	Ref.
					K	MPa		
54	PTFE	0.36203	3480.01	882.16	603–645	0–40	7.69	11
55	PPFE(typ Y)	0.44219	1997.36	962.80	298–373	0–40	0.09	38
56	PPFE(typ Z)	0.44332	2058.76	848.77	298–373	0–40	0.08	38
57	PPFE(S-20)	0.44588	2296.20	891.99	273–333	0–180	10.38	45
58	PPFE(S-65)	0.45151	2142.73	957.68	293–333	0–170	9.67	45
59	PPES	0.65739	4245.75	1739.67	513–623	0–200	0.06	30
60	PSF	0.71999	4060.52	1576.46	533–613	0–200	0.96	12
61	PPE	0.78910	3257.46	1341.98	373–593	0–200	0.04	14
62	PET	0.67743	4115.30	1466.01	533–613	0–200	1.25	15
63	PBT	0.70963	4173.54	1357.01	508–578	0–200	0.11	48
64	PHENOXY	0.77556	4268.46	1452.01	373–573	0–180	10.96	13
65	PARYL	0.73862	3729.07	1595.02	453–573	0–180	1.40	13
66	PEEK	0.69477	3827.80	1513.35	618–678	0–200	0.80	40
67	PC	0.74355	3678.78	1473.31	423–613	0–180	6.76	13
68	POM	0.69935	4055.60	1370.31	458–500	0–200	0.41	33
69	PEO	0.79605	3732.88	1222.47	353–393	0–40	7.72	31
70	PEO	Did not find a solution			353–443	0.1		47
71	PEO	0.78667	3980.36	1166.01	333–393	0–40	0.01	46
72	PEO	0.81058	3530.69	1249.51	373–473	10–80	0.06	46
73	PEO	0.79856	4082.92	1260.70	353–400	0–200	0.01	30
74	PDMS(8800)	0.88395	1837.45	1012.88	293–353	0–200	4.26	32
75	PDMS(30500)	0.87167	2018.69	978.49	293–353	0–200	13.73	32
76	PDMS(162)	1.01388	1765.84	724.84	298–343	0–90	7.68	6
77	PDMS(594)	0.90532	1788.82	867.54	298–343	0–90	3.13	6
78	PDMS(958)	0.90040	1861.19	919.72	298–343	0–90	2.46	6
79	PDMS(1540)	0.88391	1907.57	941.47	298–343	0–90	2.22	6
80	PDMS(4170)	0.87088	1979.56	953.21	298–343	0–90	1.65	6
81	PDMS(6560)	0.87152	1927.75	975.15	298–343	0–90	1.86	6
82	PDMS(7860)	0.87155	1925.44	977.21	298–343	0–90	1.88	6
83	PEtS(626)	0.90621	2738.46	1116.92	313–373	0–200	6.34	27
84	PEtS(1617)	0.89336	2627.25	1228.46	313–373	0–200	9.01	27
85	PEtS-2	0.92860	2579.46	1005.99	313–373	0–200	5.33	25
86	OCS(XC-2-1)	0.85889	2134.71	1114.76	292–574	0–50	115.00	37
87	OCS(XC-2-1 BB)	0.85834	2448.46	1145.80	292–574	0–50	872.00	37
88	OFS(FC-T-5)	0.77356	2375.62	1031.06	292–574	0–50	174.00	37
89	EPR	1.10712	2263.61	1494.71	413–523	0–62	21.93	41
90	BS(25)	0.98681	2118.36	1439.47	343–373	0–100	0.02	18
91	BS(48)	0.94826	2632.85	1474.57	343–373	0–100	0.01	18
92	BS(70)	0.92668	3108.86	1687.88	343–373	0–100	0.01	18
93	SBS(25.4)	0.98066	2678.81	1456.99	343–373	0–100	0.01	18
94	SBS(30)	0.98357	2612.82	1484.52	343–373	0–100	0.01	18
95	EVA18	1.10712	2522.83	1343.69	403–507	0–180	21.93	20
96	EVA25	1.01414	2437.71	1332.65	403–507	0–180	4.95	20
97	EVA28	1.00619	2582.40	1316.28	403–517	0–180	3.87	20
98	EVA40	0.96090	2582.06	1325.42	412–508	0–100	3.97	20
99	EVA22	1.03369	2483.09	1598.21	398–498	0–200	0.10	19
100	EVA32	1.03214	2441.49	1703.14	398–498	0–200	0.17	19
101	EVA42	0.97774	2740.05	1557.66	398–498	0–200	0.35	19
102	EVA09	1.00448	3020.10	1138.59	373–473	10–80	0.09	46
103	EVA20	0.99365	1898.35	1358.99	353–422	5–40	0.02	46
104	EVA28	0.97057	2581.43	1217.89	373–437	10–80	0.13	43
105	EVA-wax	1.03184	2586.59	1557.08	398–443	58–392	0.02	28

Abbreviations: See footnote to Table I.

the PVT surface with the given minimum value of SSQ/N. Generally, both eos fit the great majority of the data within experimental uncertainties and also with comparable quality. There are examples where COR-eos does slightly better and there are examples where BH-eos does so. Four data sets lead to $SSQ/N > 100$ with both eos (nos. 23 and 86–88) where one could conclude that the data may be of lower quality. In comparison with the error in volume-only fitted parameters for the COR-eos (see Ref. 54), an improvement in SSQ/N of about a few percent and changes of the characteristic parameters of less than 10% can be obtained in most cases. These differences decrease if $\sigma(V_i)$ is chosen smaller, but no systematic changes could be observed.

A somewhat different behavior of COR- and BH-eos is found with respect to problems arising during fitting normal pressure PVT data. Here, BH-eos causes more problems in finding an initial guess for the parameters even if one has a useful guess at higher pressure (in Ref. 50, a grid search procedure was established to solve this problem). On the other hand, if one finds a sufficient good initial guess for

the parameters of the COR-eos, special problems with atmospheric pressure data did not occur.

In further comparison of BH-eos and COR-eos and their application to PVT data of polymer melts, it is interesting to note that there is a rather strong correlation between their values of $V_{0,spec}$. From Figure 1 one can deduce a ratio of about 2/3 for $V_{0,spec}^{COR} / V_{0,spec}^{BH}$. The linear least-square line through the data is given by

$$V_{0,spec}^{COR} = 0.046196 + 0.6904 V_{0,spec}^{BH} \qquad (9)$$

with a correlation coefficient of 0.9816.

This reflects the fact that both V_0 are understood as being hard-core volumes at closest packing (extrapolated liquid state to $T = 0$ K). Surprisingly, there is also a reasonable correlation between both reducing parameters for the temperature (Fig. 2), where one can find a ratio of about 0.3 for T_{COR}^* / T_0^{BH} (which is near half of what was found for the hard-core volumes). The linear least-square line through the data is given by
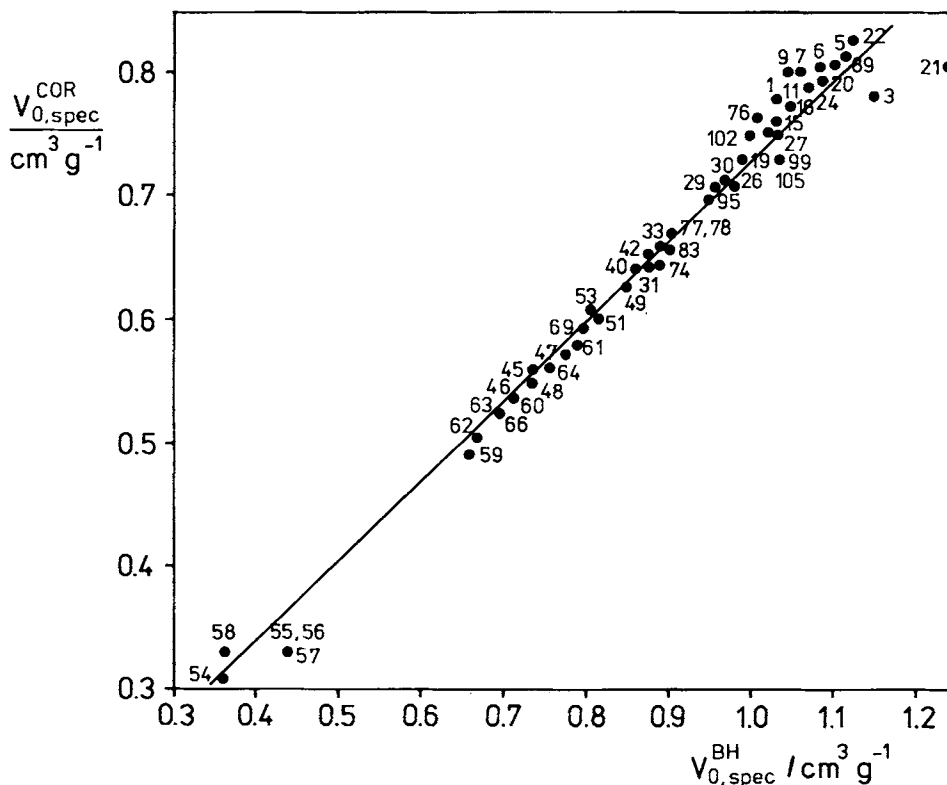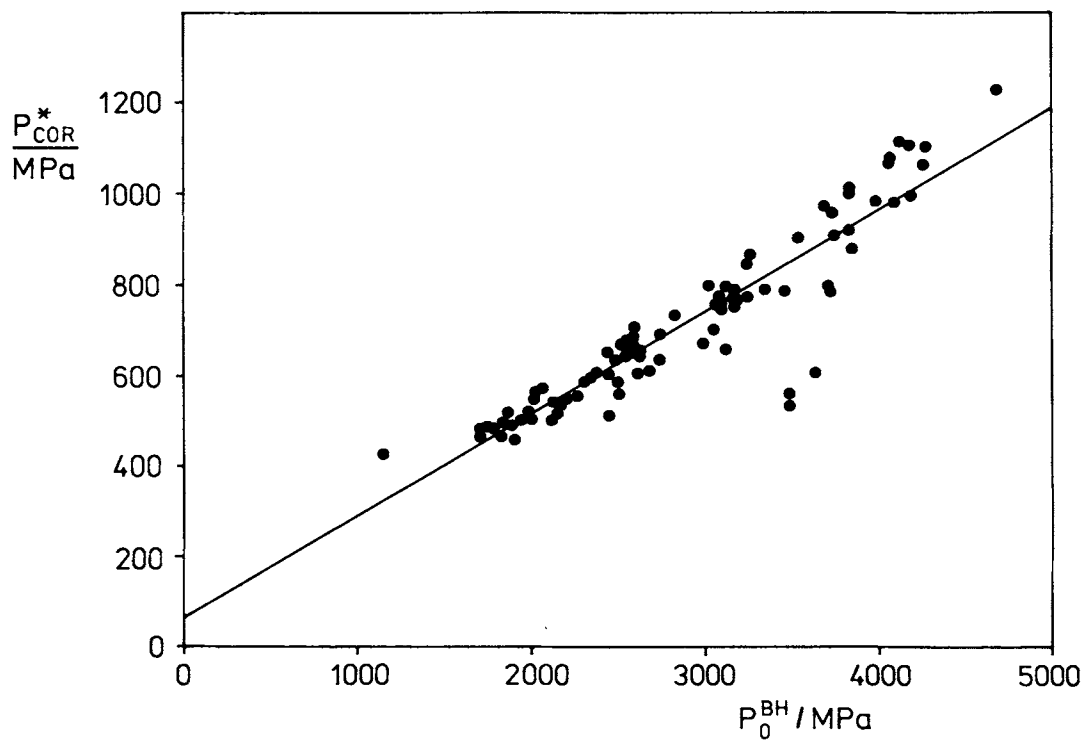

Figure 1   Correlation between the hard-core volumes of COR- and BH-eos (please note that several numbers are not included because they coincide with other polymers or simply space is missing in the diagram).
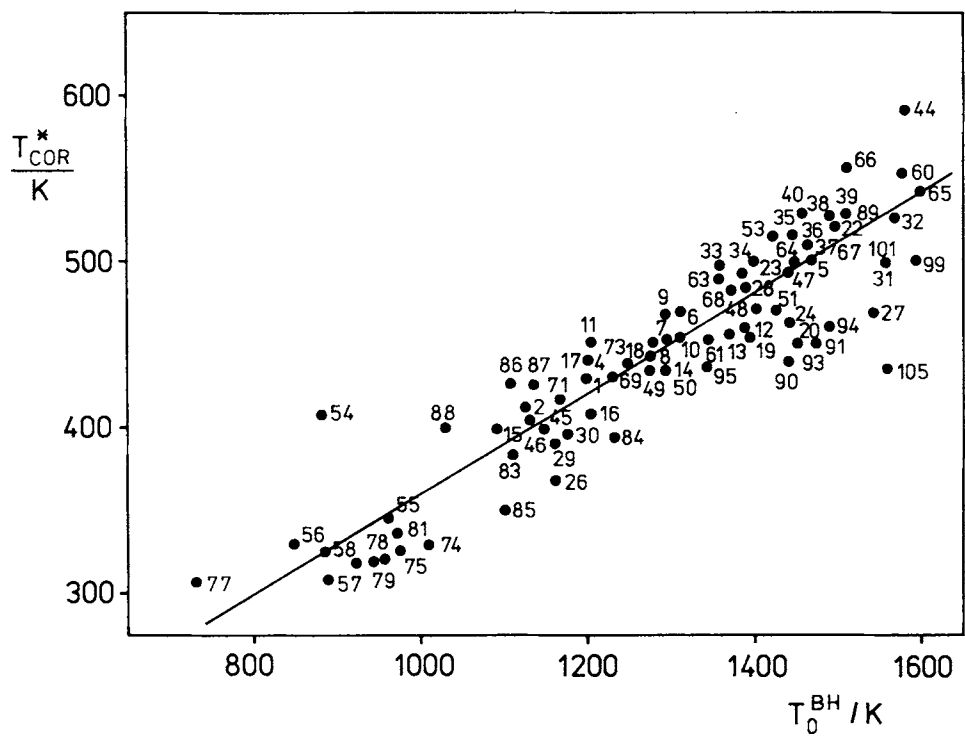
Figure 2   Correlation between the reducing temperatures of COR- and BH-eos (please note remark in Figure 1 legend).

Figure 3   Correlation between P_0 from BH-eos and a P^* parameter for the COR-eos (please note remark in figure 1 legend).

$$T^*_{COR} = 93.26943 + 0.27140 T^{BH}_0 \qquad (10)$$

with a correlation coefficient of 0.7958.

There is no such good correlation between c^{COR}_{spec} and P^{BH}_0. Only the more or less nonpolar polymers follow a certain proportionality between both parameters. Following a suggestion made by one of the reviewers of this paper, a reducing pressure is formed as a combination of all three COR-eos characteristic parameters from a simple dimensional analysis:

$$P^*_{COR} = cRT^*/V_0 \qquad (11)$$

which is in analogy to the reducing pressure of the so-called perturbed-hard-chain (PHC) eos developed by Prausnitz and his group.[63] The correlation of P^*_{COR} with P^{BH}_0 is shown in Figure 3. The least-square line through the data is given by

$$P^*_{COR} = 64.70104 + 0.22489 P^{BH}_0 \qquad (12)$$

with a correlation coefficient of 0.9218.

All three correlation coefficients would shift somewhat closer to 1 if some particular parameter combinations were neglected. But these combinations do not belong to the same polymers for all three correlations [e.g., nos. 57, 60, or 89 show the poorest correlation with eq. (12) but are good with eq. (9)]. Further work has to be done concerning the backgrounds of the above correlations, which may also bring insight into this question.

SYNOPSIS AND CONCLUSIONS

An extensive PVT data base for polymer melts[49] was used to determine the characteristic (or reducing) parameters of two different theoretical equations-of-state: the COR-eos and the BH-eos. All parameter sets were obtained by applying an error in the all-variables method, which was recently developed and applied to 11 polymers by Hartmann et al.[50] Both eos were proven to be able to describe the PVT surface of more than 100 polymers with comparable average deviations. Strong correlations between the characteristic parameters for pressure, volume, and temperature of both eos could be found, which show their interdependence in the sense of the principle of corresponding states. The results stimulate further research. Especially, it should be worthwhile to look at the derivatives of the volume: compressibility and the thermal expansion coefficient.

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