

# Pressure–Volume–Temperature Relationships for Poly(vinylidene fluoride) and Polyamide-11

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## SYNOPSIS

Experimental specific volume data as a function of temperature (30–269°C) and pressure (0–2000 bar) are presented for two semicrystalline polymers, namely, poly(vinylidene fluoride) and polyamide-11. Data for the melt state were used to determine the characteristic parameters for six theoretical equations of state as well as the empirical Tait equation. The theories employed were the cell models of Flory–Orwoll–Vrij, of Prigogine et al., and of Dee and Walsh, the lattice-fluid theory of Sanchez and Lacombe, the hole theory of Simha and Somcynsky, and the semiempirical model of Hartmann and Haque. Solid-state data were also fit using the Hartmann–Haque and Tait equations. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Pressure–volume–temperature (PVT) behavior for polymeric materials is a subject of considerable importance to polymer scientists and engineers, particularly from a process design standpoint. For example, data for the specific volume as a function of temperature and pressure provide useful information to the engineer for the analysis of forming operations as well as material properties at end-use conditions. Equally important is the need for equations of state that adequately describe this behavior over a wide range of temperature and pressure. Polymer scientists can use this information in their studies of the melt, glass, and secondary transitions and for comparison with theoretical equations of state. A recent review<sup>1</sup> of this subject gave a summary of PVT data available from the literature for 43 homopolymers and 13 copolymers in the liquid state (i.e., above the melting point for crystalline polymers or above the glass transition for amorphous polymers). It also gave a useful compendium of the characteristic parameters for six different equations of state, as well as parameters for the empirical Tait equation for the 56 polymers. However, it was mentioned that

published data for several common commercial polymers were lacking. This article presents data for two such materials, namely, the semicrystalline polymers poly(vinylidene fluoride) and polyamide-11. Characteristic parameters for the melt state are determined for the cell models of Flory–Orwoll–Vrij,<sup>2</sup> of Prigogine et al.,<sup>3,4</sup> and of Dee and Walsh,<sup>5,6</sup> as well as for the lattice-fluid theory of Sanchez and Lacombe,<sup>7,8</sup> the hole theory of Simha and Somcynsky,<sup>9</sup> the semiempirical model of Hartmann and Haque,<sup>10,11</sup> and the empirical Tait equation. Characteristic parameters for the solid state are also given for the Hartmann–Haque and Tait equations.

## EXPERIMENTAL PVT MEASUREMENTS

The polymers used in this work were poly(vinylidene fluoride) (PVDF) ( $M_n = 4.2 \times 10^5$ ,  $M_w/M_n = 2.38$ ) and polyamide-11 (PA-11) ( $M_n = 3.2 \times 10^4$ ,  $M_w/M_n = 1.94$ ). Both semicrystalline products are available commercially from Atochem (Paris-La Défense, France) under the trade names Forafon® (grade 50 LD) and Rilsan® (grade BESNO TL+), respectively. These particular grades are without a plasticizer. Relevant physical properties are given in Table I. Both products were dried and kept in a vacuum oven until use.

The densities of the polymers at 23°C and atmospheric pressure were specified by the manufacturer as 1.76 g/cm<sup>3</sup> for PVDF and 1.04 g/cm<sup>3</sup> for

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**Table I Physical Properties of Polymers Used in PVT Measurements**

Property	PVDF	PA-11
Type of sample	Compression-molded plaque	As delivered pellets
Density at 23°C <sup>a</sup>	1.76 g/cm <sup>3</sup>	1.04 g/cm <sup>3</sup>
Melting temperature <sup>b</sup>	169°C	191°C
Degree of crystallinity <sup>b</sup>	51%	24%

<sup>a</sup> Manufacturer's specification; verified with a Mettler balance and density determination kit.

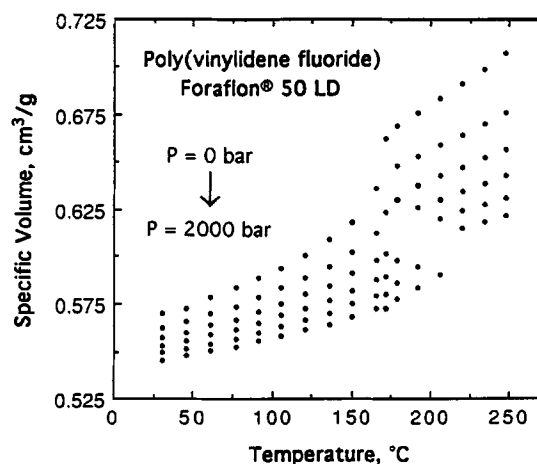
<sup>b</sup> Determined by DSC.  $\Delta H_f^0$  for 100% crystalline samples: PVDF 100 J/g and PA-11 229 J/g.

PA-11. These values were verified with a Mettler AE240 balance and density determination kit (ME-33360) using both distilled water and toluene as immersion liquids. The densities at 23°C and atmospheric pressure were subsequently used as a point of reference as explained below. Relative changes in specific volume as a function of temperature and pressure were then measured by using a PVT apparatus, which has been fully described elsewhere.<sup>12</sup> These measurements were performed by the author in the laboratory of chemical engineering of Professor I. C. Sanchez at the Center for Polymer Research of The University of Texas at Austin. The apparatus consists of a sample cell containing about 1–1.5 g of the sample and mercury as a confining fluid. A flexible bellows closes off one end of the cell. The movement of the bellows on changing temperature or pressure is used to calculate the volume change of the sample cell, having been first calibrated to “zero” at 30°C and 100 bar. In the isothermal mode, volume readings are obtained at fixed-pressure intervals (usually increments of 50–100 bar) at a constant temperature. Values of the relative volume change with pressure are then extrapolated to  $P = 0$  using the Tait equation relationship, giving  $\Delta V(T, P = 0)$ . After measurements along an isotherm, the temperature is changed by 8–10°C and the process is repeated. The absolute accuracy of the device is  $(1-2) \times 10^{-3}$  cm<sup>3</sup>/g; however, volume changes as small as  $(1-2) \times 10^{-4}$  cm<sup>3</sup>/g can be resolved. To convert the relative volume changes to absolute values of specific volume, the values of  $\Delta V(T, P = 0)$  are extrapolated to a temperature where the specific volume (or density) is known for the material, in this case 23°C. The difference between the known absolute specific volume and the relative volume change at that temperature is then added as a con-

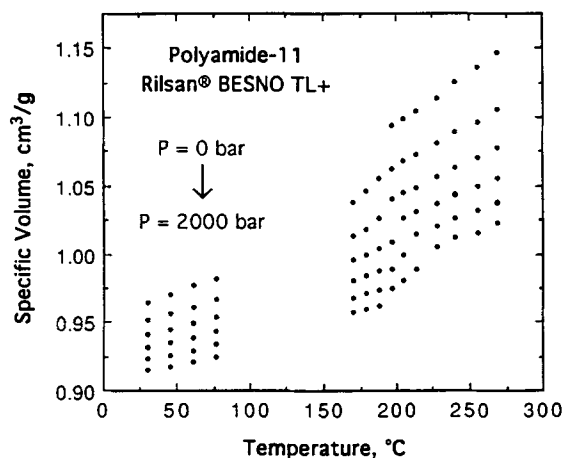
stant to all measured relative values. A version of this PVT apparatus is available as a complete instrument from Gnomix Research, Boulder, Colorado.

It is very important to evacuate all air from the sample cell before filling it with mercury. This is for the obvious reason that air is much more compressible than either the solid polymer sample or the confining mercury. The extremely sensitive measurements of volume change will be greatly affected by the presence of air in the sample cell. With pelletized polymer samples, such as is the case for PA-11, the evacuation of air is generally not a problem. However, it is much more difficult to be sure of complete evacuation with powdered samples. Therefore, it is necessary to first make a compression-molded plaque and then cut small pieces from it to use as the PVT sample. This technique was used for PVDF.

PVT measurements were made covering both the melt and solid-state regions for each polymer. For each isotherm, the pressure was systematically increased from 100 to 2000 bar in increments of 50–100 bar. The temperature ranges of the measurements on PVDF were 30–150°C for the solid state and 178–248°C for the melt; those for PA-11 were 30–179°C for the solid state and 205–269°C for the melt. The measured specific volumes as a function of temperature and pressure are presented graphically in Figures 1 and 2 for PVDF and PA-11, respectively. For clarity of presentation, not all the data points are shown in the figures. (Numerical



**Figure 1** PVT data for PVDF (Forafion® 50 LD) covering the semicrystalline solid and melt states. The actual data (given in Table II) are from 100 to 2000 bar by 100 bar increments; however, for clarity, only data from 0 to 2000 bar by 400 bar increments are shown. The data at 0 bar are an extrapolation using the Tait equation.



**Figure 2** PVT data for PA-11 (Rilsan® BESNO TL+) covering the semicrystalline solid and melt states. The actual data (given in Table III) are from 100 to 2000 bar by 100 bar increments; however, for clarity, only data from 0 to 2000 bar by 400 bar increments are shown. The data at 0 bar are an extrapolation using the Tait equation.

values of all obtained data are given in Tables II and III. The dotted lines in these tables demark the melting transition as a function of pressure.) For a given isotherm, the points increase in a downward direction (i.e., specific volume decreases with increasing pressure) from  $P = 0$  to  $P = 2000$  bar in increments of 400 bar.

No previous literature data could be found for PA-11. The present data for PVDF can, however, be compared to previously published data obtained at atmospheric pressure only.<sup>13</sup> In that study, the specific volume was measured using a specific-gravity bottle with silicone oil as a medium. Measurements were made on the liquid phase at different temperatures between 180 and 240°C and on an annealed compression-molded specimen at temperatures between 20 and 160°C. Differences between their specific-volume measurements and this work vary from 0.002 to 0.003 cm<sup>3</sup>/g over the melt temperature range and from 0.010 to 0.021 cm<sup>3</sup>/g over the solid-state temperature range, with their values being consistently lower. For the melt state, these differences are probably on the order of the experimental error of their specific-gravity bottle measurements, which is presumed to be larger than the experimental error of the PVT apparatus employed in this work. However, the differences for the solid state are significantly larger than could be explained by experimental error in the measurements. This can be attributed to the higher degree of crystallinity of their sample. Nakagawa and Ishida<sup>13</sup> estimated a degree of crystallinity for their annealed sample

of about 60% by X-ray diffraction, compared with 51% for the *unannealed* PVDF sample used in the present PVT measurements. (Annealing of this sample at 155°C for 7 days increased the degree of crystallinity to about 61%.) Also, the number-average molecular weight of their sample ( $M_n = 6.4 \times 10^4$ ) was less than the PVDF used here.

Although the data presented in Figures 1 and 2 cover a wide pressure range, the relatively limited temperature ranges place restrictions on the direct interpolation and/or extrapolation to other conditions, especially for the melt. Furthermore, it is somewhat cumbersome to determine the various thermodynamic derivatives (isobaric thermal expansion, isothermal compressibility, and isochoric thermal pressure coefficients) as a function of temperature and pressure. This problem can be avoided by using a mathematical representation of the data, which permits the analytical determination of specific volume or its thermodynamic derivatives at a specified temperature and pressure. Two different types of mathematical representations will be discussed in the next section, namely, the empirical Tait equation and theoretical equations of state.

## MATHEMATICAL REPRESENTATIONS OF PVT DATA

### The Tait Equation

Perhaps the most common empirical representation of polymeric PVT data is that of the Tait equation.<sup>14</sup> It is, in fact, an isothermal compressibility model (i.e., a volume–pressure relationship). The general form of the Tait equation is

$$V(P, T) = V(0, T) \times \{1 - C \ln[1 + P/B(T)]\} \quad (1)$$

where the coefficient  $C$  is usually taken to be a universal constant equal to 0.0894.<sup>15</sup> The zero-pressure isotherm  $V(0, T)$  is usually given by

$$V(0, T) = V_0 \exp(\alpha T) \quad (2)$$

where  $\alpha$  is the thermal expansion coefficient. The Tait parameter  $B(T)$  is usually given by

$$B(T) = B_0 \exp(-B_1 T) \quad (3)$$

Thus, the Tait equation is normally a four-parameter ( $V_0, \alpha, B_0, B_1$ ) representation of the experimental PVT data. In some cases, eqs. (2) and (3) do not fit the data accurately and polynomial expressions are used:

**Table II Experimental PVT Data for Poly(vinylidene fluoride) (PVDF) (Forafion® 50 LD)**

<i>P</i>	Specific Volume (cm <sup>3</sup> /g) at <i>T</i> (°C):								
	30.5	46.1	61.3	77.5	91.3	106.0	121.0	136.3	150.1
0	0.5699	0.5726	0.5782	0.5834	0.5883	0.5936	0.6002	0.6085	0.6183
100	0.5680	0.5708	0.5760	0.5808	0.5856	0.5908	0.5970	0.6046	0.6139
200	0.5659	0.5690	0.5735	0.5779	0.5826	0.5878	0.5937	0.6006	0.6094
300	0.5641	0.5672	0.5717	0.5758	0.5804	0.5854	0.5910	0.5975	0.6057
400	0.5626	0.5656	0.5699	0.5737	0.5784	0.5832	0.5885	0.5945	0.6024
500	0.5611	0.5641	0.5683	0.5718	0.5764	0.5811	0.5861	0.5918	0.5993
600	0.5598	0.5628	0.5668	0.5701	0.5745	0.5790	0.5838	0.5893	0.5964
700	0.5586	0.5614	0.5651	0.5685	0.5728	0.5770	0.5817	0.5868	0.5937
800	0.5573	0.5601	0.5638	0.5669	0.5711	0.5752	0.5779	0.5846	0.5911
900	0.5562	0.5589	0.5625	0.5654	0.5696	0.5735	0.5779	0.5825	0.5886
1000	0.5553	0.5577	0.5611	0.5641	0.5681	0.5718	0.5761	0.5805	0.5864
1100	0.5542	0.5566	0.5599	0.5628	0.5665	0.5702	0.5744	0.5786	0.5840
1200	0.5531	0.5556	0.5587	0.5615	0.5651	0.5687	0.5726	0.5768	0.5821
1300	0.5522	0.5545	0.5576	0.5602	0.5638	0.5673	0.5710	0.5751	0.5802
1400	0.5511	0.5535	0.5564	0.5590	0.5625	0.5658	0.5695	0.5734	0.5783
1500	0.5501	0.5523	0.5553	0.5578	0.5611	0.5645	0.5680	0.5718	0.5766
1600	0.5492	0.5514	0.5542	0.5566	0.5599	0.5631	0.5666	0.5701	0.5749
1700	0.5483	0.5504	0.5532	0.5555	0.5586	0.5618	0.5652	0.5687	0.5733
1800	0.5474	0.5495	0.5522	0.5545	0.5575	0.5606	0.5638	0.5671	0.5717
1900	0.5465	0.5485	0.5510	0.5533	0.5563	0.5593	0.5624	0.5658	0.5700
2000	0.5457	0.5476	0.5501	0.5522	0.5551	0.5582	0.5612	0.5644	0.5684
	165.0	171.4	178.3	192.0	206.4	219.9	234.2	248.1	
0	0.6356	0.6623	0.6687	0.6756	0.6835	0.6911	0.6986	0.7073	
100	0.6289	0.6500	0.6627	0.6691	0.6764	0.6832	0.6901	0.6978	
200	0.6229	0.6421	0.6566	0.6627	0.6693	0.6757	0.6820	0.6884	
300	0.6177	0.6326	0.6519	0.6577	0.6639	0.6698	0.6756	0.6817	
400	0.6127	0.6233	0.6476	0.6531	0.6590	0.6644	0.6699	0.6758	
500	0.6083	0.6161	0.6436	0.6489	0.6544	0.6595	0.6648	0.6703	
600	0.6042	0.6113	0.6397	0.6449	0.6499	0.6551	0.6600	0.6653	
700	0.6010	0.6049	0.6359	0.6414	0.6460	0.6509	0.6557	0.6608	
800	0.5979	0.6014	0.6304	0.6379	0.6424	0.6471	0.6518	0.6566	
900	0.5950	0.5983	0.6175	0.6347	0.6389	0.6435	0.6480	0.6528	
1000	0.5923	0.5952	0.6065	0.6317	0.6357	0.6402	0.6444	0.6492	
1100	0.5896	0.5921	0.6022	0.6290	0.6328	0.6372	0.6414	0.6458	
1200	0.5873	0.5893	0.5977	0.6262	0.6300	0.6341	0.6383	0.6425	
1300	0.5850	0.5868	0.5947	0.6236	0.6272	0.6314	0.6355	0.6395	
1400	0.5831	0.5845	0.5916	0.6179	0.6247	0.6288	0.6329	0.6367	
1500	0.5811	0.5822	0.5888	0.6001	0.6222	0.6262	0.6303	0.6339	
1600	0.5792	0.5801	0.5863	0.5942	0.6198	0.6238	0.6278	0.6313	
1700	0.5773	0.5782	0.5840	0.5904	0.6170	0.6215	0.6253	0.6287	
1800	0.5756	0.5763	0.5819	0.5879	0.6112	0.6192	0.6229	0.6262	
1900	0.5738	0.5744	0.5795	0.5855	0.6000	0.6170	0.6205	0.6238	
2000	0.5721	0.5726	0.5775	0.5833	0.5899	0.6148	0.6183	0.6215	

*P* in Bar.

$$V(0, T) = a_0 + a_1T + a_2T^2 \quad (4)$$

$$B(T) = b_0 + b_1T + b_2T^2 \quad (5)$$

The Tait equation has been applied successfully to both polymer melts and solids [with different

values of the coefficients in eqs. (2)–(5) for the melt and solid states of the same material]. This author, in a recent review of equations of state for polymer liquids, has provided a compilation of the Tait equation parameters for 56 homo- and copolymers.<sup>1</sup> Ta-

Table III Experimental PVT Data for Polyamide-11 (PA-11) (Rilsan® BENSO TL+)

P	Specific Volume (cm <sup>3</sup> /g) at T (°C):												
	30.4	45.8	61.5	76.2	170.3	179.3	188.2	197.0	204.9	213.6	227.3	240.5	
0	0.9638	0.9702	0.9769	0.9825	1.0376	1.0460	1.0555	1.0945	1.0986	1.1049	1.1145	1.1253	
100	0.9605	0.9663	0.9725	0.9784	1.0308	1.0384	1.0472	1.0854	1.0900	1.0959	1.1050	1.1151	
200	0.9569	0.9621	0.9677	0.9745	1.0237	1.0304	1.0392	1.0758	1.0815	1.0868	1.0956	1.1051	
300	0.9541	0.9589	0.9640	0.9706	1.0182	1.0244	1.0322	1.0691	1.0745	1.0798	1.0880	1.0969	
400	0.9514	0.9556	0.9606	0.9670	1.0130	1.0187	1.0258	1.0625	1.0681	1.0728	1.0809	1.0896	
500	0.9486	0.9526	0.9574	0.9636	1.0083	1.0135	1.0198	1.0566	1.0619	1.0663	1.0743	1.0828	
600	0.9461	0.9498	0.9544	0.9603	1.0037	1.0085	1.0143	1.0507	1.0560	1.0604	1.0679	1.0761	
700	0.9436	0.9471	0.9514	0.9571	0.9994	1.0041	1.0092	1.0455	1.0505	1.0548	1.0621	1.0700	
800	0.9412	0.9441	0.9487	0.9541	0.9955	0.9997	1.0044	1.0404	1.0453	1.0492	1.0565	1.0643	
900	0.9388	0.9417	0.9459	0.9512	0.9916	0.9956	0.9999	1.0355	1.0403	1.0442	1.0512	1.0587	
1000	0.9365	0.9393	0.9432	0.9484	0.9879	0.9917	0.9956	1.0294	1.0356	1.0395	1.0463	1.0534	
1100	0.9342	0.9370	0.9407	0.9457	0.9843	0.9880	0.9918	1.0182	1.0312	1.0350	1.0415	1.0485	
1200	0.9320	0.9347	0.9384	0.9431	0.9808	0.9845	0.9879	1.0094	1.0269	1.0305	1.0369	1.0436	
1300	0.9297	0.9325	0.9360	0.9404	0.9776	0.9810	0.9843	1.0032	1.0226	1.0264	1.0326	1.0392	
1400	0.9277	0.9303	0.9337	0.9382	0.9744	0.9778	0.9808	0.9978	1.0165	1.0225	1.0285	1.0351	
1500	0.9254	0.9283	0.9314	0.9357	0.9713	0.9746	0.9773	0.9937	1.0065	1.0186	1.0245	1.0308	
1600	0.9234	0.9260	0.9292	0.9334	0.9682	0.9714	0.9741	0.9892	0.9999	1.0148	1.0205	1.0269	
1700	0.9215	0.9240	0.9272	0.9310	0.9653	0.9684	0.9708	0.9852	0.9936	1.0110	1.0167	1.0230	
1800	0.9196	0.9220	0.9251	0.9290	0.9624	0.9654	0.9677	0.9818	0.9891	1.0055	1.0131	1.0192	
1900	0.9175	0.9200	0.9230	0.9267	0.9595	0.9624	0.9647	0.9783	0.9850	0.9956	1.0093	1.0154	
2000	0.9156	0.9181	0.9210	0.9246	0.9568	0.9596	0.9617	0.9747	0.9813	0.9890	1.0058	1.0118	

P in Bar.

**Table IV Tait Equation Parameters for PVDF and PA-11 in the Melt and Solid States**

Polymer	Temp Range	$V(P, T) = V(0, T)\{1 - 0.0894 \ln[1 + P/B(T)]\}$		Avg $\Delta V$ ( $10^4 \text{ cm}^3/\text{g}$ )
		$V(0, T) (\text{cm}^3/\text{g})^a$	$B(T) (\text{bar})^a$	
PVDF	30–150	$0.5660 + 7.988 \times 10^{-5} t + 1.747 \times 10^{-6} t^2$	$4247 \exp(-7.654 \times 10^{-3} t)$	8.8
	178–248	$0.5790 \exp(8.051 \times 10^{-4} t)$	$2440 \exp(-5.210 \times 10^{-3} t)$	8.5
PA-11	30–179	$0.9515 \exp(4.247 \times 10^{-4} t)$	$3026 \exp(-5.063 \times 10^{-3} t)$	6.2
	205–269	$0.9581 \exp(6.664 \times 10^{-4} t)$	$2547 \exp(-4.178 \times 10^{-3} t)$	4.2

<sup>a</sup> The temperature  $t$  is in °C. The equation is valid for pressures up to 2000 bar.

ble IV summarizes the values of the Tait equation coefficients for the two new polymers presented here in both the melt and solid states. These coefficients when used in eqs. (2)–(5) are able to reproduce the experimental specific volume data to within  $\pm 0.0009 \text{ cm}^3/\text{g}$  in the case of PVDF and  $\pm 0.0005 \text{ cm}^3/\text{g}$  in the case of PA-11.

### Theoretical Equations of State

Equation-of-state theories offer the possibility of predicting thermodynamic properties and behavior for pure polymers as well as for polymer blends and solutions. These statistical thermodynamic models start with an expression for the Gibbs free energy and derive all other thermodynamic properties, e.g., the equation of state  $V(P, T) = \partial G / \partial P|_T$ .

An equation of state is a mathematical representation of a substance's volumetric behavior as a function of pressure and temperature. These equations are often given in "reduced" variables, i.e., the state variables of volume, pressure, and temperature are "reduced" or made dimensionless by forming a ratio with a characteristic parameter of the same dimensional units. Thus, the following dimensionless variables are defined:

$$\tilde{P} \equiv P/P^*, \quad \tilde{v} \equiv v/v^*, \quad \tilde{T} \equiv T/T^* \quad (6)$$

where  $P^*$ ,  $v^*$ , and  $T^*$  are the "reducing" or characteristic parameters. Most satisfy the principle of corresponding states, i.e., the equations of state in reduced variables are considered as universal functions for all polymer liquids. The PVT behavior in terms of the real thermodynamic variables for individual materials are obtained from the relations in eq. (6) and their three characteristic parameters.

There are a very large number of equations of state in the literature, most of which are applicable only to polymer melts (cf. Flory–Orwoll–Vrij,<sup>2</sup> Dee and Walsh,<sup>5,6</sup> Simha and Somcynsky,<sup>9</sup> Hartmann

and Haque,<sup>10,11</sup> and Sanchez and Lacombe<sup>7,8</sup>). They differ in the form of the intermolecular potential energy function (hard sphere, Lennard-Jones, etc.) and in the mathematical formalism for deriving the conformational energy and entropy (cell, lattice, and hole theories) from statistical thermodynamics. The semiempirical equation of state of Hartmann and Haque (HH) is also applicable to polymer solids,<sup>11</sup> although, as with the Tait equation, the characteristic parameters for the solid state are different from those for the melt. Table V presents a summary of the six equations of state used in this work. These theories have been reviewed and compared elsewhere.<sup>1</sup> Readers are directed to the original references to have a complete derivation of each theory.

### CHARACTERISTIC EQUATION-OF-STATE PARAMETERS

A standard nonlinear least-squares regression method was used to simultaneously fit the three characteristic parameters for each equation of state to the actual experimental PVT data. The minimization function used in the least-squares regression is  $\sum (P_{\text{exp}} - P_{\text{calc}})^2$ . The fitted characteristic parameters were then used to calculate the average deviation from the experimental specific volume as  $\sum |(v_{\text{exp}} - v_{\text{calc}})|/N$ , where  $N$  is the number of data points. Since the accuracy of the fits are better over a restricted data range and since often one only needs data and thermodynamic functions at low pressures for engineering work, the characteristic parameters were fit over a pressure range of 0–500 bar as well as over the full 0–2000 bar range.

Characteristic parameters for the six equations of state over the low- and full-pressure ranges are given for each polymer in Table VI. The average deviation in specific volume is also given in each case.

**Table V Six Common Equations of State for Polymeric Liquids**

Cell models

Flory-Orwoll-Vrij<sup>2</sup>

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)} - \frac{1}{\tilde{T}\tilde{v}}$$

$$\tilde{P} = P/P^*, \tilde{v} = v/v^*, \tilde{T} = T/T^*$$

Prigogine et al.<sup>3,4</sup> (square-well approximation)

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 0.8909)} - \frac{2}{\tilde{T}} \left( \frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4} \right)$$

$$\tilde{P} = P/P^*, \tilde{v} = v/v^*, \tilde{T} = T/T^*$$

Dee and Walsh<sup>5,6</sup> (modified cell model)

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 0.8909q)} - \frac{2}{\tilde{T}} \left( \frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4} \right)$$

$$\tilde{P} = P/P^*, \tilde{v} = v/v^*, \tilde{T} = T/T^* \quad (q = 1.07)$$

Lattice-fluid models

Sanchez and Lacombe<sup>7,8</sup>

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = -\tilde{v}[\ln(1 - 1/\tilde{v}) + 1/\tilde{v}] - \frac{1}{\tilde{T}\tilde{v}}$$

$$\tilde{P} = P/P^*, \tilde{v} = v/v^*, \tilde{T} = T/T^*$$

or equivalently,

$$\tilde{\rho} = 1 - \exp[-(\tilde{\rho}^2 + \tilde{P})/\tilde{T} - \tilde{\rho}]$$

$$\tilde{P} = P/P^*, \tilde{\rho} = \rho/\rho^*, \tilde{T} = T/T^* \quad (\tilde{\rho} = 1/\tilde{v})$$

Hole models

Simha and Somcynsky<sup>9</sup>

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{y\tilde{v}^{1/3}}{[(y\tilde{v})^{1/3} - 0.8909y]} - \frac{2y}{\tilde{T}} \left( \frac{1.2045}{(y\tilde{v})^2} - \frac{1.011}{(y\tilde{v})^4} \right)$$

$$\tilde{P} = P/P^*, \tilde{v} = v/v^*, \tilde{T} = T/T^*$$

with

$$(s/3c)[1 + y^{-1} \ln(1 - y)]$$

$y =$  fraction of occupied sites;  $(s/3c) = 1$  in normal practice

$$= - \frac{\left[ \frac{1}{3}(y\tilde{v})^{1/3} - 0.8909y \right]}{[(y\tilde{v})^{1/3} - 0.8909y]} - \frac{y}{6\tilde{T}} \left( \frac{2.409}{(y\tilde{v})^2} - \frac{3.033}{(y\tilde{v})^4} \right)$$

The two equations must be solved simultaneously

Semiempirical models

Hartmann and Haque<sup>10,11</sup>

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v}$$

$$\tilde{P} = P/B_0, \tilde{v} = v/v_0, \text{ and } \tilde{T} = T/T_0$$

A comparison of the performance of the six equations of state in fitting the experimental melt specific volume data for PVDF and PA-11 shows the same trends as observed for the 56 polymer liquids studied previously.<sup>1</sup> At low pressures (0–500 bar), the average deviation from experimental specific volume for the two polymers was less than  $\pm 0.0005 \text{ cm}^3/\text{g}$

for all six equations of state. (Overall average deviations for the 56 polymers at low pressures varied in the range of  $\pm 0.0004$ – $0.0010 \text{ cm}^3/\text{g}$ .) These values are near the accuracy limits of the experimental measurements, with no major difference in the performance of the six equations of state. However, as expected, the overall average deviation over the

Table VI Characteristic Equation-of-State Parameters for PVDF and PA11

Polymer	Temperature Range (°C)	For $P = 0-500$ bar				For $P = 0-2000$ bar			
		$P^*$ (bar)	$T^*$ (K)	$v^*$ (cm <sup>3</sup> /g)	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)	$P^*$ (bar)	$T^*$ (K)	$v^*$ (cm <sup>3</sup> /g)	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)
<u>Flory-Orwoll-Vrij</u>									
PVDF	178-248	5,512	7,400	0.5244	2.5	5,761	7,225	0.5200	4.4
PA11	205-269	5,668	8,204	0.8742	3.6	5,896	7,710	0.8582	15.0
<u>Prigogine CM</u>									
PVDF	178-248	5,797	4,368	0.5750	3.8	6,715	4,415	0.5747	8.7
PA11	205-269	6,199	4,815	0.9560	3.6	6,822	4,803	0.9533	6.4
<u>Dee and Walsh MCM</u>									
PVDF	178-248	5,874	5,656	0.5402	3.3	6,471	5,718	0.5406	5.9
PA11	205-269	6,198	6,268	0.8999	3.0	6,518	6,226	0.8973	3.5
		$P^*$ (bar)	$T^*$ (K)	$\rho^*$ (g/cm <sup>3</sup> )	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)	$P^*$ (bar)	$T^*$ (K)	$\rho^*$ (g/cm <sup>3</sup> )	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)
<u>Sanchez-Lacombe</u>									
PVDF	178-248	4,508	694	1.7229	2.7	4,885	665	1.7496	7.4
PA11	205-269	4,654	765	1.0351	4.7	5,114	703	1.0635	20.2
		$P^*$ (bar)	$T^*$ (K)	$v^*$ (cm <sup>3</sup> /g)	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)	$P^*$ (bar)	$T^*$ (K)	$v^*$ (cm <sup>3</sup> /g)	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)
<u>Simha-Somcynsky</u>									
PVDF	178-248	7,990	10,130	0.5927	4.5	9,022	10,440	0.5964	9.1
PA11	205-269	8,345	11,410	0.9925	3.7	9,068	11,450	0.9917	5.9
		$B_0$ (bar)	$T_0$ (K)	$v_0$ (cm <sup>3</sup> /g)	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)	$B_0$ (bar)	$T_0$ (K)	$v_0$ (cm <sup>3</sup> /g)	Avg $\Delta v$ (10 <sup>4</sup> cm <sup>3</sup> /g)
<u>Hartmann-Haque</u>									
PVDF	30-150					47,300	1,457	0.5191	13.7
	178-248	29,370	1,245	0.5381	4.9	31,190	1,308	0.5454	7.1
PA11	30-179					38,410	1,925	0.9064	7.4
	205-269	31,340	1,405	0.9011	4.1	31,580	1,456	0.9101	5.6

wider pressure range increases for all equations, and differences between the theories become apparent. This effect was more noticeable for PA-11 than for PVDF. Four theories, the Simha-Somcynsky hole theory, the Dee and Walsh modified cell model, the Prigogine cell model, and the Hartmann and Haque model, were found to maintain excellent fitting capabilities with overall average deviations in the range of  $\pm 0.0004-0.0009$  cm<sup>3</sup>/g. These models achieve the same performance with three parameters that the empirical Tait equation provides with four.

The Flory-Orwoll-Vrij and Sanchez-Lacombe lattice-fluid theories were found to suffer a significant loss in performance over the wider pressure range, with overall average deviations in the range of  $\pm 0.0015-0.0020$  cm<sup>3</sup>/g.

The Hartmann-Haque equation of state has the advantage of being applicable to the solid state as well as to the melt. The average deviation from experimental specific volume for PVDF and PA-11 is larger for the solid state ( $\pm 0.0007-0.0014$  cm<sup>3</sup>/g) than for the melt ( $\pm 0.0006-0.0008$  cm<sup>3</sup>/g), although



it is still on the order of experimental error. This is consistent with Hartmann and Haque's results for other semicrystalline polymers.<sup>11</sup> For glassy amorphous polymers, they showed a similar or slightly better fit to experimental data in the solid state than in the melt.

The results of this study on PVDF and PA-11 support the previous conclusions concerning equation-of-state performance in fitting polymer liquid PVT data.<sup>1</sup> The Dee and Walsh modified cell model and the Simha-Somcynsky hole model give the best fit over a wide range of temperature and pressure, with the Sanchez-Lacombe lattice-fluid theory being consistently less accurate. The semiempirical Hartmann and Haque model also appears to offer good performance while being mathematically simpler than either the MCM or SS model.

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