

Heat Capacity of Polymer Melts from the Polymer Chain-of-Rotators Equation of State

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ABSTRACT: Recently, the chain-of-rotators equation of state derived from the rotational partition function was extended to polymers. Values of the three equation of state (EOS) parameters were obtained from fitting with experimental pressure–volume–temperature data and the parameters were correlated with the structure of the polymer repeat unit. In this article, the residual molar heat capacity derived from an EOS is added to the ideal gas heat capacity from Benson's group contribution method to obtain the polymer molar heat capacity at constant pressure, C_p . Predictions from the polymer chain-of-rotators (PCOR) using correlated parameters are compared with those obtained from PCOR, Sanchez–Lacombe, Flory–Orwoll–Vrij, and the perturbed-hard-sphere chain equations of state using parameters fitted from experimental data. Deviations of calculated C_p from the formula of van Krevelen for liquid polymers are likewise presented. With the correlations developed for its parameters, the PCOR offers the advantage of predicting the C_p for polymer melts from just the knowledge of the polymer's structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 841–848, 1998

Key words: heat capacity; chain-of-rotors equation of state; polymer

INTRODUCTION

Knowledge of thermal effects is important for polymer manufacture and processing, and consequently the heat capacity at constant pressure, C_p , is of interest. The experimental method generally used in the polymer melt region is adiabatic scanning calorimetry. In cases when such experimental capability or literature data are unavailable, a plausible alternative is to obtain a good estimate from an equation of state for polymers.

A general method in the calculation of molar heat capacity is to combine the ideal gas C_p with the residual C_p

$$C_p = C_p^{\text{ideal gas}} + C_p^{\text{resid}} \quad (1)$$

where the ideal gas term can be obtained from additivity of group contributions by the method of Benson.¹

The residual heat capacity can be derived from an equation of state (EOS) using the following thermodynamic relations

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (2)$$

where U is the molar internal energy, V is the molar volume, S is the molar entropy, P is the pressure, and T is the temperature. Integrating eq. (2) gives the residual internal energy, U^{resid} , in terms of the EOS variables P , V , and T .

$$U^{\text{resid}} = \int_{\infty}^V \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad (3)$$

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The residual molar heat capacity at constant volume is determined by differentiating the U^{resid} expression given in eq. (3) with respect to T .

$$C_V^{\text{resid}} = \left(\frac{\partial U^{\text{resid}}}{\partial T} \right)_V = \int_{\infty}^V \left[T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \right] dV \quad (4)$$

The residual molar heat capacities at constant pressure and constant volume are, in turn, related by

$$C_P^{\text{resid}} = C_V^{\text{resid}} - \frac{T(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \quad (5)$$

where R is the ideal gas constant. Substituting eq. (4) into eq. (5) gives C_P^{resid} as a function of the partial derivatives of pressure with respect to temperature and volume.

$$C_P^{\text{resid}} = \int_{\infty}^V \left[T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \right] dV - \frac{T(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \quad (6)$$

The above derivation for the molecular C_p^{resid} holds for any EOS. For polymers, the property of interest is the C_p per repeat unit, that is, the segmental C_p . This can be obtained by dividing eq. (6) by the number of segments in the polymer chain, n . In the limit of large n , the term involving R in the segmental C_p^{resid} becomes insignificant compared with the other terms.

$$C_p^{\text{resid}}(\text{segment}) = \frac{1}{n} \int_{\infty}^V \left[T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \right] dV - \frac{T(\partial P/\partial T)_V^2}{n(\partial P/\partial V)_T} \quad (7)$$

HEAT CAPACITY FROM EQUATIONS OF STATE

The Polymer Chain-of-Rotators (PCOR) EOS

The PCOR EOS for a large degree of polymerization, n , is given in segmental form as a sum of the rotational and attractive contributions,²

$$\frac{Pv}{RT} = \frac{c}{2}(\alpha - 1) \left[\frac{3y + 3\alpha y^2 - (\alpha + 1)y^3}{(1 - y)^3} \right] - \frac{a}{RT(v + b)} \quad (8)$$

where v is the segmental molar volume, $y = b/4v$ is the packing fraction of the polymer segment; a , b , and c are the attractive, excluded volume and effective rotational degrees of freedom parameters for a polymer segment, and α is the nonsphericity constant (1.078). The attractive parameter a varies linearly with temperature in the PCOR EOS

$$a = a_0 + a_1 T \quad (9)$$

while the parameters b and c are constant for a polymer. The parameters a_0 , a_1 , b , and c for 26 polymers obtained from fitting with experimental PVT data were reported by Sy-Siong-Kiao, Caruthers, and Chao.² The PCOR parameters used in this work that were fitted from experimental PVT data are given in Table I.

Correlations were also developed to estimate the PCOR parameters from the structure of the polymer repeat unit. For a detailed discussion of the correlation schemes for parameters a , b , and c , the reader is referred to ref. 2. The PCOR parameters correlated from chemical structure for the polymers in this article are given in Table II.

Since it is the desired property for polymers, C_p^{resid} refers to the segmental, rather than the molecular, residual heat capacity for the remainder of this article. Using eq. (8) in eq. (7) yields the following expression for C_p^{resid} from the PCOR EOS

$$C_p^{\text{resid}} = \frac{\left\{ \frac{RTc(\alpha - 1)}{2v} \left[\frac{3y + 3\alpha y^2 - (\alpha - 1)y^3}{(1 - y)^3} \right] - \frac{a_1}{v(v + b)} \right\}^2}{\frac{3RTc(\alpha - 1)}{2v^2} \times \left[\frac{2y + 3\alpha y^2 - 4/3(\alpha + 1)y^3}{(1 - y)^3} \right]}$$

Table I PCOR Parameters from Fitting Experimental PVT Data

Polymer	$\alpha_0 \times 10^{-4}$ (cm ⁶ bar mol ⁻²)	$\alpha_1 \times 10^{-4}$ (cm ⁶ bar mol ⁻² K ⁻¹)	b (cm ³ /mol)	c
Polyethylene, high density	1348.08	-1.2096	83.28	1.5300
Polypropylene	1876.92	-1.0579	131.98	1.3499
Poly(1-butene)	4656.51	-4.4707	178.71	1.5499
Polyisobutylene	4074.89	-3.2551	172.62	1.1726
Poly(<i>cis</i> -1,4 butadiene)	3768.71	-1.4263	154.04	2.8600
Poly(4-methyl-1-pentene)	8714.70	-6.6668	262.16	3.0131
Polystyrene	11126.55	-5.5588	264.42	3.2176
Poly(vinyl chloride)	2935.29	-0.2406	115.07	2.9286
Poly(vinyl acetate)	7998.34	-6.2709	176.70	5.6997
Poly(methyl methacrylate)	11689.99	-11.8739	233.50	2.0102
Poly(<i>n</i> -butyl methacrylate)	24014.58	-25.5469	373.16	3.3391
Polytetrafluoroethylene	2000.32	-1.9552	118.19	1.9018
Poly(ethylene terephthalate)	48726.37	-44.4750	364.46	9.6600
Poly(ethylene glycol)	2829.04	-2.4519	100.51	2.6771
Polytetrahydrofuran	6585.48	-6.1984	200.69	1.9876
Polyamide-6	24401.56	-22.4948	288.76	4.2347
Polycarbonate	78402.78	-62.2432	556.80	9.0323
Poly(ether ether ketone)	118589.70	-124.2332	601.11	7.5400
Polysulfone	238805.18	-191.8224	968.42	11.5309

$$+ \frac{3y^2 + 3\alpha y^3 - (\alpha + 1)y^4}{(1 - y)^4} \left] - \frac{a}{v(v + b)} \left[\frac{1}{v + b} + \frac{1}{v} \right] \quad (10)$$

Sanchez—Lacombe (S-L) EOS

Sanchez and Lacombe³ developed an EOS for polymer liquids based on the lattice framework with empty sites. As the number of lattice sites occupied by an r -mer becomes large, the S-L equation reduces to

$$\frac{1}{\tilde{V}^2} + \tilde{P} + \tilde{T} \left[\ln \left(1 - \frac{1}{\tilde{V}} \right) + \frac{1}{\tilde{V}} \right] = 0 \quad (11)$$

where

$$\tilde{V} = \frac{V}{V^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{T} = \frac{T}{T^*}$$

and V^* , P^* , and T^* are the required reducing parameters. The three parameters were obtained by least-squares fitting with experimental PVT

data. The S-L EOS parameters reported by Rodgers⁴ are used in this article. The residual C_p derived from eq. (11) is given below.

$$C_p^{\text{resid}} = -\tilde{T} \left(\frac{P^* V^* MW_{\text{segment}}}{T^*} \right) \times \frac{\left[\ln \left(1 - \frac{1}{\tilde{V}} \right) + \frac{1}{\tilde{V}} \right]^2}{\frac{\tilde{T}}{\tilde{V}^2(1 - \tilde{V})} + \frac{2}{\tilde{V}^3}} \quad (12)$$

where the MW_{segment} term is included as V^* is usually given in literature as mass specific volume.

Flory—Orwoll—Vrij (F-O-V) EOS

The equation of state for chain molecules developed by Flory, Orwoll, and Vrij⁵ in reduced form is given as

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{(\tilde{V}^{1/3} - 1)} - \frac{1}{\tilde{V}\tilde{T}} \quad (13)$$

where

Table II PCOR Parameters from Chemical Structure Correlation

Polymer	$a_0 \times 10^{-4}$ (cm ⁶ bar mol ⁻²)	$a_1 \times 10^{-4}$ (cm ⁶ bar mol ⁻² K ⁻¹)	b (cm ³ /mol)	c
Polyethylene, high density	1403.24	-1.3040	84.90	1.5538
Polypropylene	3027.45	-2.8387	127.32	1.7375
Poly(1-butene)	5134.15	-4.8190	169.78	2.4680
Polyisobutylene	4988.97	-4.6822	167.74	1.7828
Poly(<i>cis</i> -1,4 butadiene)	4727.06	-4.4370	155.21	2.8188
Poly(4-methyl-1-pentene)	11650.85	-10.9498	254.64	3.3368
Polystyrene	14794.03	-13.9106	260.83	3.5366
Poly(vinyl chloride)	3513.58	-3.2974	121.39	1.5256
Poly(vinyl acetate)	8464.95	-7.9550	190.40	2.4535
Poly(methyl methacrylate)	11657.83	-10.9588	232.82	2.4467
Poly(<i>n</i> -butyl methacrylate)	25017.15	-23.5320	360.18	5.0171
Polytetrafluoroethylene	1777.31	-1.6471	127.24	1.4056
Poly(ethylene terephthalate)	37074.81	-34.8893	390.85	5.4394
Poly(ethylene glycol)	2448.95	-2.2966	100.26	2.2781
Polytetrahydrofuran	6915.99	-6.4962	185.17	3.8318
Polyamide-6	23623.59	-22.2261	294.36	5.2217
Polycarbonate	73966.19	-69.6291	565.27	6.8756
Poly(ether ether ketone)	99773.29	-93.9384	618.60	10.0068
Polysulfone	243131.21	-228.9715	961.35	13.6006

$$\tilde{V} = \frac{V}{V^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{T} = \frac{T}{T^*}$$

and V^* , P^* , and T^* are the required reducing parameters. The F-O-V EOS parameters obtained by Rodgers⁴ from fitting with experimental PVT data are used in this work. The C_p^{resid} obtained from eq. (13) is as follows

$$C_p^{\text{resid}} = -\tilde{T} \left(\frac{P^* V^* MW_{\text{segment}}}{T^*} \right) \times \frac{\left(\frac{1}{\tilde{V} - \tilde{V}^{2/3}} \right)^2}{\left[\frac{2}{\tilde{V}^3} + \frac{(2 - 3\tilde{V}^{1/3})\tilde{T}}{3\tilde{V}^{1/3}(\tilde{V} - \tilde{V}^{2/3})^2} \right]} \quad (14)$$

As in the S-L EOS, the MW_{segment} term corrects for the units of V^* which is usually given as mass specific volume.

Perturbed Hard-Sphere Chain (PHSC) EOS

Song, Lambert, and Prausnitz⁶ combined a modified Chiew⁷ equation of state for hard-sphere chains with the van der Waals attractive pertur-

bation term to obtain the perturbed hard-sphere-chain EOS. In the limit of very large number of segments (which were assumed to be effective hard spheres) in a polymer chain, the PHSC EOS in reduced form is given by

$$\tilde{P} = - \frac{\mathcal{F}_a(\tilde{T}/s_\infty)}{\tilde{V}^2} - \tilde{T} \left[\frac{g(d^+)}{\tilde{V}} - \frac{1}{\tilde{V}} - \frac{\mathcal{F}_b(\tilde{T}/s_\infty)g(d^+)}{\tilde{V}^2} \right] \quad (15)$$

where

$$\tilde{P} = \frac{P}{P^*}, \quad P^* = 3\epsilon/2\pi\sigma^3$$

$$\tilde{T} = \frac{T}{T^*}, \quad T^* = \epsilon/k$$

$$\tilde{V} = \frac{V}{V^*}, \quad V^* = RT^*(r/M)/P^*$$

The parameters σ , ϵ/k , and r/M for several polymers were obtained⁶ from fitting with experimental PVT data. The procedure described to correlate the PHSC parameters from chemical structure is not used in this article as only an approximate

correlation was obtained, especially for polymers with complex repeat unit.⁶

The pair radial distribution function of hard spheres at contact, $g(d^+)$, is taken from the Carnahan–Starling equation

$$g(d^+) = \frac{1 - \eta/2}{(1 - \eta)^3} \quad (16)$$

where the packing fraction $\eta = \mathcal{F}_b(\tilde{T}/s_\infty)/4\tilde{V}$. The universal functions \mathcal{F}_b and \mathcal{F}_a were fitted from thermodynamic properties of argon and methane.

$$\mathcal{F}_b(\tilde{T}/s_\infty) = \beta_1 e^{-\beta_2 \tilde{T}/s_\infty} + (1 - \beta_1)[1 - e^{-\beta_3(\tilde{T}/s_\infty)^{-1/4}}] \quad (17)$$

$$\mathcal{F}_a(\tilde{T}/s_\infty) = \alpha_1 + \alpha_2 e^{-\alpha_3 \tilde{T}/s_\infty} \quad (18)$$

where $\beta_1 = 0.5849$, $\beta_2 = 0.4772$, $\beta_3 = 1.0669$, $\alpha_1 = 0.7117$, $\alpha_2 = 1.9003$, $\alpha_3 = 0.5152$, and $s_\infty = 7.0701$.

For high molecular weight polymers, the C_p^{resid} derived from Eq. 15 is

$$C_p^{\text{resid}} = - \left(\frac{P^* V^* MW_{\text{segment}}}{T^*} \right) \times \left[\int_{\tilde{V}}^{\infty} \tilde{T} \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{T}^2} \right) d\tilde{V} + \tilde{T} \left(\frac{\partial \tilde{P} / \partial \tilde{T}}{\partial \tilde{P} / \partial \tilde{V}} \right)_{\tilde{T}} \right] \quad (19)$$

where

$$\begin{aligned} \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_{\tilde{V}} &= - \frac{1}{\tilde{V}^2} \frac{d\mathcal{F}_a(\tilde{T}/s_\infty)}{d\tilde{T}} + \frac{1}{\tilde{V}} \\ &+ g(d^+) \left[- \frac{1}{\tilde{V}} + \frac{\mathcal{F}_b(\tilde{T}/s_\infty)}{\tilde{V}^2} \right. \\ &+ \left. \frac{\tilde{T}}{\tilde{V}^2} \frac{d\mathcal{F}_b(\tilde{T}/s_\infty)}{d\tilde{T}} \right] \\ &+ \frac{\tilde{T}}{\tilde{V}} \frac{\partial g(d^+)}{\partial \tilde{T}} \left[\frac{\mathcal{F}_b(\tilde{T}/s_\infty)}{\tilde{V}} - 1 \right] \end{aligned} \quad (20)$$

$$\begin{aligned} \left(\frac{\partial \tilde{P}}{\partial \tilde{V}} \right)_{\tilde{T}} &= \frac{2\mathcal{F}_a(\tilde{T}/s_\infty)}{\tilde{V}^3} - \frac{\tilde{T}}{\tilde{V}^2} \\ &+ g(d^+) \left[\frac{\tilde{T}}{\tilde{V}^2} - \frac{2\tilde{T}\mathcal{F}_b(\tilde{T}/s_\infty)}{\tilde{V}^3} \right] \\ &+ \frac{\tilde{T}}{\tilde{V}} \frac{\partial g(d^+)}{\partial \tilde{V}} \left[\frac{\mathcal{F}_b(\tilde{T}/s_\infty)}{\tilde{V}} - 1 \right] \end{aligned} \quad (21)$$

$$\begin{aligned} &\tilde{T} \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{T}^2} \right) \\ &= - \frac{\tilde{T}}{\tilde{V}^2} \frac{\partial^2 \mathcal{F}_a}{\partial \tilde{T}^2} \\ &+ \tilde{T} \frac{\partial g(d^+)}{\partial \tilde{T}} \left[- \frac{1}{\tilde{V}} + \frac{\mathcal{F}_b}{\tilde{V}^2} + \frac{\tilde{T}}{\tilde{V}^2} \frac{d\mathcal{F}_b(\tilde{T}/s_\infty)}{d\tilde{T}} \right] \\ &+ \tilde{T} g(d^+) \left[\frac{2}{\tilde{V}^2} \frac{d\mathcal{F}_b(\tilde{T}/s_\infty)}{d\tilde{T}} + \frac{\tilde{T}}{\tilde{V}^2} \frac{d^2 \mathcal{F}_b(\tilde{T}/s_\infty)}{d\tilde{T}^2} \right] \\ &+ \frac{\tilde{T}}{\tilde{V}} \frac{\partial g(d^+)}{\partial \tilde{T}} \left[\frac{\mathcal{F}_b(\tilde{T}/s_\infty)}{\tilde{V}} - 1 \right] \\ &+ \frac{\tilde{T}^2}{\tilde{V}} \frac{\partial^2 g(d^+)}{\partial \tilde{T}^2} \left[\frac{\mathcal{F}_b(\tilde{T}/s_\infty)}{\tilde{V}} - 1 \right] \\ &+ \frac{\tilde{T}}{\tilde{V}} \frac{\partial g(d^+)}{\partial \tilde{T}} \frac{d\mathcal{F}_b(\tilde{T}/s_\infty)}{d\tilde{T}} \end{aligned} \quad (22)$$

Unlike the other EOS considered in this study, the semi-infinite integral in eq. (19) does not vanish for the PHSC EOS. Numerical integration using an IMSL FORTRAN subroutine was therefore implemented.

EMPIRICAL CORRELATION FOR HEAT CAPACITY OF POLYMER LIQUIDS

Van Krevelen⁸ assumed the molar heat capacity of liquid polymers is a linear function of temperature. The experimental C_p at 298 K along with the slope of the C_p versus temperature plot are required in the formula.

$$\frac{1}{C_{p,298}} \frac{dC_p}{dT} = k \quad (23)$$

where k is a constant determined by fitting experimental molar heat capacity data. Values of k for a number of polymers were reported. A mean value of 1.2×10^{-3} was suggested for polymers when experimental data are not available. In the comparisons presented below, the general value of 1.2×10^{-3} was used.

RESULTS AND DISCUSSION

Nineteen polymers of various types, from the simplest nonbranched and nonsubstituted homogeneous backbone of polyethylene to the heavily branched and substituted heterogeneous backbone of polysulfone, have been selected to test the EOS predictions of heat capacity. Heat capacity data were compared with the calculated C_p from the PCOR, Sanchez-Lacombe, Flory-Orwoll-Vrij, and perturbed hard-sphere chain EOS along with those calculated from the formula of Van Krevelen. The ideal gas heat capacities were obtained from an updated table of Benson's group contributions given in Reid, Prausnitz and Poling.⁹ As the group values are provided only in 100 K or 200 K increments from 300 to 1000 K, curve-fitting of the ideal gas heat capacity as a smooth function of temperature was done to obtain the intermediate values. Table III presents the average absolute percent deviations of the equations from data for the nineteen polymers. Detailed comparison is shown with two examples that represent simple and more complex chemical structures of the repeat unit, polypropylene in Figure 1 and polysulfone in Figure 2.

The overall average deviations were similar for all the EOS, ranging from 5% for the PHSC to a little over 8% for the Sanchez-Lacombe. The van Krevelen formula gave an overall deviation close

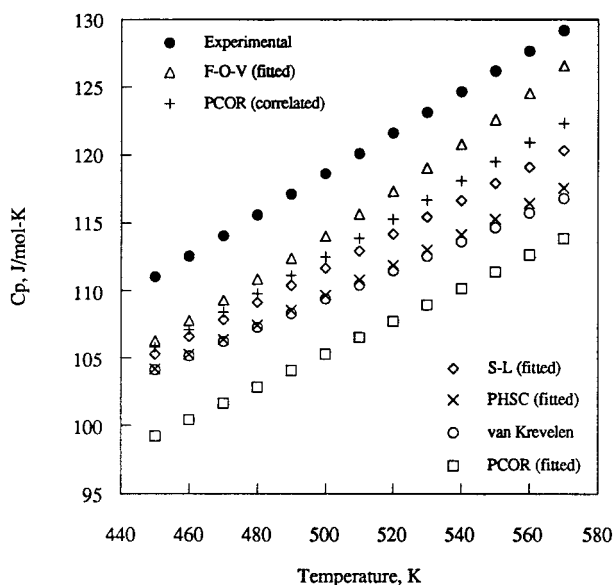


Figure 1 Heat capacity of polypropylene. Experimental data are taken from Gaur and Wunderlich (ref. 16).

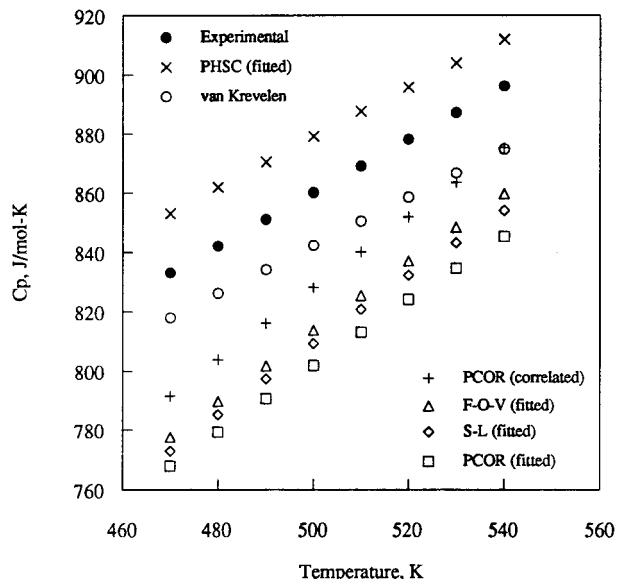


Figure 2 Heat capacity of polysulfone. Experimental data are taken from Varma-Nair and Wunderlich (ref. 19).

to 6%. Using the parameters correlated with chemical structure, however, the PCOR yielded generally better predictions compared with those of PCOR, S-L, and F-O-V EOS using parameters fitted from PVT data. For the majority of the polymers investigated, the PHSC EOS and the formula of van Krevelen gave better results than those from PCOR using both fitted and correlated parameters. The PHSC and van Krevelen's formula likewise gave deviations of < 5% for 10 (of 18) and 12 (of 19) polymers, respectively, compared with 7 (of 19) for the PCOR using correlated parameters. The integral of the second partial derivative of P with T from the PHSC is non-zero and cannot be analytically evaluated. For the PHSC EOS, numerical integration up to the ideal gas limit of infinite V is required to obtain C_p ; thus, it may be more difficult to use in practice. The van Krevelen formula, on the other hand, is not predictive in the sense that it requires as input the heat capacity data at 298 K.

The PCOR allows prediction of the molar heat capacity of polymer melts solely from their chemical structure, that is, the Benson group contributions to the ideal gas C_p and the EOS parameters correlated with the characteristic quantities of the repeat unit. This is of interest in the design of new polymers where it may be desirable to estimate the physical properties before the polymer is synthesized.

Table III Average Absolute Percent Deviation of Molar Heat Capacity of Polymer Melts from Equations of State

Polymer	Temperature (K)	Average Absolute Deviation (%)							Data Source (Reference Number)
		PCOR EOS (Fitted Parameters)	S-L EOS (Fitted Parameters)	F-O-V EOS (Fitted Parameters)	PHSC EOS (Fitted Parameters)	PCOR EOS (Correlated Parameters)	van Krevelen C_p Formula		
Polyethylene, high density	420–470	4.76	6.37	7.30	2.82	4.15	4.90	10	
Polypropylene	450–570	11.29	6.00	3.51	7.70	5.12	7.99	11	
Poly(1-butene)	410–510	4.87	3.11	3.26	0.90	2.54	2.28	12	
Polyisobutylene	320–380	1.19	1.50	1.20	4.26	3.21	0.12	12	
Poly(cis-1,4 butadiene)	290–330	7.98	5.06	1.33	4.40	2.58	0.65	12	
Poly(4-methyl-1-pentene)	520–540	11.96	9.63	8.52	8.29	8.15	11.61	12	
Polystyrene	380–470	10.86	8.90	9.80	5.71	4.96	3.39	13	
Poly(vinyl chloride)	360–380	18.77	16.51	17.69	12.17	14.37	20.07	12	
Poly(vinyl acetate)	330–370	6.62	8.29	7.38	0.81	9.33	2.90	12	
Poly(methyl methacrylate)	380–470	8.53	8.01	8.74	5.01	8.60	2.27	14	
Poly(n-butyl methacrylate)	300–450	6.79	5.59	5.50	3.54	5.79	15.13	14	
Polytetrafluoroethylene	600–650	2.36	4.31	0.87	7.21	5.12	1.51	12	
Poly(ethylene terephthalate)	550–590	10.64	15.97	14.18	0.88	16.58	6.96	15	
Poly(ethylene glycol)	330–490	8.09	12.28	10.83	1.64	9.37	4.48	16	
Polytetrahydrofuran	330–360	12.77	13.27	12.15	6.22	9.77	0.90	17	
Polyamide-6 ^a	490–590	9.52	17.03	18.10		8.61	13.48	15	
Polycarbonate	430–560	7.46	7.31	6.59	0.90	7.09	0.18	18	
Poly(ether ether ketone)	620–680	6.32	3.71	1.23	14.63	0.60	7.98	19	
Polysulfone	470–540	6.67	5.83	5.27	2.13	3.58	2.08	19	
Average		8.29	8.35	7.55	4.96	6.82	5.73		

^a No parameters were reported for the perturbed hard-sphere-chain EOS.

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