Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. III. Polyoxides

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The heat capacity of poly(oxymethylene), poly(oxyethylene), poly(oxytrimethylene), poly(oxytetramethylene), poly(oxyoctamethylene), poly(oxypropylene), poly(oxymethyleneoxyethylene), poly(oxymethyleneoxytetramethylene), poly(oxy-1,4-phenylene), poly(oxy-2,6-dimethyl-1,4-phenylene), poly(oxy-2,6-diphenyl-1,4-phenylene) and poly[oxy-2,2-bis(chloromethyl)trimethylene] is reviewed on the basis of measurements on 35 samples reported in the literature. The crystallinity dependence is critically evaluated and a set of recommended data for each polyoxide is derived. Entropy, enthalpy, and Gibbs energy functions are calculated. The data have been compared to that of polyethylene and the contribution of –O– group has been evaluated. This paper is the third in a series which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: Crystal; crystallinity; density; enthalpy; entropy; fusion; Gibbs energy; glass transition; heat capacity; linear macromolecule; poly(oxymethylene)s; poly(oxyphenylene)s; poly(oxypropylene).

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1. Introduction

This is the third paper in a series of discussions on the heat capacity of linear macromolecules. In the first paper [1][1], the heat capacity of selenium, a model compound for a monoatomic, linear macromolecule was analyzed. In the second paper [2], the heat capacity of polyethylene, the simplest organic linear macromolecule was analyzed. In this paper all the polyoxides on which heat capacity data are available have been analyzed. These are poly(oxymethylene), poly(oxypropylene), poly(oxyethylene), poly(oxytrimethylene), poly(oxytetramethylene), poly(oxyoctamethylene), poly(oxymethyleneoxyethylene), poly(oxymethyleneoxytetramethylene), poly(oxypropylene), poly(oxy-1,4-phenylene), poly(oxy-2,6-dimethyl-1,4-phenylene), poly(oxy-2,6-diphenyl-1,4-phenylene) and poly[oxy-2,2-bis(chloromethyl)trimethylene]. From the series of unsubstituted polyoxides of the type $(CH_2-)_n O-$, the heat capacity contribution of –O– group has been evaluated by comparison with polyethylene. In the subsequent publications, the analysis of heat capacities of groups of more complicated linear macromolecules will be reported and heat capacity contributions of other structural groups will be evaluated.

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[1] Numbers in brackets refer to the literature references in section 5.

[2] See AIP document no. PAPS JPCRD-10-1001-26 for 26 pages of (give brief description of material). Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N.Y. 10017. The price is $1.50 for a microfiche, or $5 for a photocopy. Airmail additional. Make checks payable to the American Institute of Physics.

2. Heat Capacity of Polyoxides

2.1. Introduction

Polyoxides derive from all-carbon-backbone polymers by occasional substitution of an O– for a CH_2– in the backbone chains. The repeating unit, formula weight, crystal structure, density, melting temperature, heat of fusion and glass transition temperature of all the polyoxides analyzed in the paper are listed in table 1.

Table 1. Crystal structures and thermal properties of polyoxides

Polyoxide (Formula wt.) structure of repeat unit	Crystal syst. Space group Mol. helix	Unit cell axes and angles	No. of units	ρ_c Mg m^{-3}	Cryst. packing density	T_m(K)	ΔH_f kJ mol^{-1}	ρ_a Mg m^{-3}	Amorp. packing density	T_g(K)
Poly(oxymethylene) I (30.03) CH_2-O-	TRIG P3 or $P3_2$ 2*9/5	4.471Å 4.471 17.39	9	1.491	0.78	457	9.79	1.25	0.65	191
Poly(oxymethylene) II (30.03) CH_2-O-	ORTH $P2_12_12_1$ 2*2/1	4.767 7.660 3.563	4	1.533	0.81					
Poly(oxyethylene) (44.05) $(CH_2-)_2O$	MONO P_c(?) 3*7/2	8.16 12.99 19.30 β=126.1°	28	1.239	0.72	342	8.66	1.13	0.65	232
Poly(oxytrimethylene) III (58.08) $(CH_2-)_3O$	ORTH $C222_1$ 8*1/1	9.23 4.82 7.21	4	1.203	0.73	308	9.44			195
Poly(oxytetramethylene) (72.10) (CH_2) O-	MONO C2/c 5*2/1	5.59 8.90 12.07 β=134.2°	4	1.12	0.70	330	14.4	0.981	0.61	189
Poly(oxyoctamethylene) PTHF-type (128.01) $(CH_2-)_8O$-	MONO C2/c 9*2/1	5.67 9.04 22.45 β=134.5°	4	1.038	0.68	347	29.3			255
Poly(oxyoctamethylene) PE-type (128.01) $(CH_2-)_8O$-	ORTH 9*2/1	7.36 4.93 22.43	4	1.046	0.69					
Poly(oxypropylene) (58.08) CH_2CHCH_3-O-	ORTH $P2_12_12_1$ 3*2/1	10.46 4.66 7.03	4	1.126	0.69	348	8.4	0.998	0.61	198
Poly(oxymethyleneoxyethylene) (74.08) $(CH_2)_2O$-CH_2-O-	TRIG P1 5*5/1	12.32 4.66 24.7 γ=100.9°	15	1.325	0.74	328	16.7			209
Poly(oxymethyleneoxytetramethylene) (102.13) $(CH_2)_4O$-CH_2-O-	ORTH $Pna2_1$ 14*1/1	8.50 4.79 13.50	4	1.234	0.74	296	14.33			189

Table 1. Crystal structures and thermal properties of polyoxides -- (Continued)

Polyoxide (Formula wt.) structure of repeat unit	Crystal syst. Space group Mol. helix	Unit cell axes and angles	No. of units	ρ_c Mg m^{-3}	Cryst. packing density	T_m(K)	ΔH_f kJ mol^{-1}	ρ_a Mg m^{-3}	Amorp. packing density	T_g(K)
Poly(oxy-1,4-phenylene) (92.10) $(C_6H_4-)O-$	ORTH Pbcn 7*2/1	8.07 5.54 9.72	4	1.408	0.74	535	7.82	1.27	0.67	358
Poly(oxy-2,6-dimethyl-1,4-phenylene) (120.15) $[C_6H_2(CH_3)_2-]O-$	TETR 7*	11.92 11.92 17.10	16	1.314	0.82	535	5.0-5.9			482
Poly(oxy-2,6-diphenyl-1,4-phenylene) (244.29) $[C_6H_2(C_6H_5)_2-]O-$	TETR $P4_12_12$ 7*4/1	12.51 12.51 17.08	8	1.214	0.70	753	12.2			493
Poly[oxy-2,2-bis(chloromethyl)trimethylene] α-form (155.02) $(CH_2-)_2-C(CH_2Cl)_2-O-$	ORTH Pnma 3*1/1	17.85 8.16 4.67	4	1.514	0.72	453-463	23-32	1.39	0.66	278

The first member of this series, poly(oxymethylene) is a highly crystalline polymer. It crystallizes well from solution and melt. In addition, it is possible to obtain extended chain crystals from gaseous, liquid and solid monomers. It exists in two crystal forms: the trigonal form [3] and the less stable, orthorhombic form [4]. The helices show successive bond rotation angles of 102° and 117°, not far from all-gauche conformations. Both crystals contain in their unit cells only helices of the same handedness; consequently a mixture of crystals with helices of different handedness is expected for both crystal forms. Melting temperatures for the trigonal poly(oxymethylene) have been reported ranging from 448 to 479 K [5,6]. Many of the high melting temperatures are most likely caused by superheating, while the lower ones are probably connected with poor crystallization. An estimate of the best experimentally determined equilibrium melting temperature is 457 K [7]. Heat of fusion was measured by Wilski [8] on melt crystallized polymer by adiabatic calorimeter and recalculated to 100% crystallinity as 9.79 ± 0.45 kJ mol^{-1}. This value agrees well with actually measured heat of fusion of needle-like crystals by Iguchi [6] (9.45 kJ mol^{-1}). Values for the glass transition temperature for poly(oxymethylene) have been reported from 188 to 263 K, with a preferred value of 191 K listed in [12].

The next member of the series of polyoxides is poly(oxyethylene). Its helix is opened up to a 3*7/2 conformation. The helix corresponds closely to a gauche, trans, trans sequence of bond rotations, with gauche conformations between the two CH_2 groups. The equilibrium melting temperature was estimated by Vidotto et al. [9] to be 342.8 K. This melting point was later verified by Kovacs and Gonthier [10]. A final analysis of melting data of 42 fractions measured in various laboratories by Buckley and Kovacs [11] gave an equilibrium melting temperature for infinite molecular weight of 342.0 ± 0.4 K. The heat of fusion was extrapolated from calorimetric measurements on various extended chain crystals to infinite molecular weight and 342 K by Buckley and Kovacs [11] to 8.66 ± 0.12 kJ mol^{-1}. Values for the glass transition temperature range from 158 to 233 K, with a preferred value of 232 listed in [12].

The third polyoxide, poly(oxytrimethylene), also called poly(oxacyclobutane), is known in three crystal modifications. All three have been determined by Tadokoro et al. [14]. As in poly(oxyethylene), the two bonds to each oxygen are in a conformation close to trans. Crystal form I is obtained on crystallization in contact with water. Its unit cell contains four water molecules. Heat capacity measurements have been reported on crystal form III only. As crystal form II transforms to crystal form III at ordinary temperatures, it is not amenable to heat capacity measurements. Yoshida, Sakiyama, and Seki [15] have estimated the melting point of crystal form III to be 308 K using adiabatic calorimetry. The heat of fusion was measured by Yoshida, Sakiyama, and Seki [15] on annealed polymer by adiabatic calorimetry and recalculated to 100% crystalline form III as 9.44 kJ mol^{-1}. It is possible to obtain completely amorphous poly(oxytrimethylene) by quenching from the melt. The glass transition temperature of amorphous poly(oxytrimethylene) is 195 K [15].

The fourth polyoxide, poly(oxytetramethylene), also called polytetrahydrofuran is the first member of this series of simple polyoxide with a planar zig-zag conformation, similar to polyethylene. The equilibrium melting temperature has been established at 330 K [7]. Lower melting temperatures of 314 K [16,17] represents the melt end of folded chain crystals and should be increased to the melting temperature for extended chain equilibrium crystals. The heat of fusion has been estimated from calorimetry of semicrystalline samples and changes of the melting temperature with pressure to be 14.4 ± 1.5 kJ mol^{-1} [7]. The glass transition of amorphous poly(oxytetramethylene) has been established reasonably well at 189 ± 1 K [17,18].

Poly(oxyoctamethylene) is the only polyoxide with long sequences of CH_2 which has been studied by heat capacity measurements. Kobayashi et al. [19] have determined the crystal structure of poly(oxyoctamethylene). According to their results, there are two crystal forms: an orthorhombic, polyethylene-like structure and a monoclinic, poly(oxytetramethylene)-like structure. Equal amounts of both crystal forms are obtained on crystallization from solution. However, only monoclinic crystal modification is obtained on melt crystallization. The heat capacity has been determined for both crystal forms. The melting temperature and the heat of fusion have been established at 347 K and 29.3 kJ mol^{-1}, respectively [20]. The glass transition is reasonably well established at 255 K [20].

Two polyoxides of the type $[-(CH_2)_x-O-(CH_2)_y O-]_n$ have been studied. These include poly(oxymethyleneoxyethylene), also called poly-1,3-dioxolan and poly(oxymethyleneoxytetramethylene), also called poly-1,3-dioxepan. They are prepared by ring opening polymerization of 1,3-dioxolan and 1,3-dioxepan, respectively. Their crystal structures [12] and related properties [23,24] are listed in table 1.

The simplest polyoxide with a side group is poly(oxypropylene). Its chemical structure is complicated by the possibility of stereo isomers. Heat capacity measurements have been reported on a largely racemic sample of low crystallinity. The crystal structure as determined by Cesari et al. [25] and related properties [12,26] are listed in table 1.

Three polyoxides with phenylene groups within the backbone chain have been analyzed for heat capacity. These are poly(oxy-1,4-phenylene), poly(oxy-2,6-dimethyl-1,4-phenylene) and poly(oxy-2,6-diphenyl-1,4-phenylene). The structure determination of poly(oxy-1,4-phenylene) by Boon and Magré [27] has shown a zig-zag chain with linear $O-C_6H_4$ elements. Their crystal structures [12,27] and related properties [12,28–30] are listed in table 1.

The last polyoxide for which heat capacities have been measured is poly[oxy-2,2-bis(chloromethyl)trimethylene]. This polymer was manufactured under the trade name of Penton. Its crystal structure for the α-form [12] and related properties [12,31] are listed in table 1.

2.2. Literature Data on Heat Capacity of Polyoxides

Twenty six investigations have been reported in the literature on the heat capacity measurement of various types of polyoxides. Heat capacities of over forty samples have been measured over wide ranges of temperature.

All investigations were critically evaluated in terms of sample characterization, experimental technique used, error limits and accuracy of representation of data. It was found that only 21 of the 26 investigations met our standards of acceptable data (discussed in ref. [1]). These investigations are listed in tables 3, 5, 8, 12, 15, 17, 20, 23, 26, 29, 32, and 35. These contain heat capacity data on 34 samples of twelve types of polyoxides. Five investigations which did not contain acceptable data were not included in further analysis. These are listed in table 2, along with brief comments on the reasons for exclusion from this study.

2.3. Recommended Data on Heat Capacity and Thermodynamic Functions of Polyoxides

2.3.1. Poly(oxymethylene)

Six investigations [32, 33, 35–38] have been reported in the literature on the heat capacity of poly(oxymethylene). Details of these investigations are given in table 3. The data which span a wide range of temperatures from 0.4 to 480 K are given in tables A1 and A2. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. All measurements are either on highly crystalline samples (samples 1, 2, 3, 8, 9, 10) or completely crystalline samples (sample 7). Thus, the calculation of the heat capacity of amorphous poly(oxymethylene) from crystallinity extrapolations using the two phase model cannot be made. The data on molten poly(oxymethylene) have been reported only for two samples with results differing by 25%. The measurements cover only a very limited temperature range because of decomposition. Thus, no estimate has been made for the heat capacity of molten or amorphous poly(oxymethylene).

To determine the recommended values of heat capacity of crystalline poly(oxymethylene) below 25 K, the data on samples 7 from 12 to 25 K, sample 9 from 0.4 to 4 K and sample 10 from 2 to 18 K were curve fitted into the equation

$$C_p = \exp[-0.092752\,(\ln T)^3 + 0.31559\,(ln T)^2 + 2.85938\,(\ln T) - 7.9883]\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (1)$$

The RMS deviation was 7.1%. Equation (1) was used to calculate the recommended values of heat capacity from 0.1 to 25 K.

From 30 K to the glass transition temperature (190 K), Seki's data on completely crystalline sample and Dainton et al.'s data on highly crystalline Delrin and trioxane copolymers were averaged to determine the recommended values of heat capacities from 30 to 190 K.

Above 190 K the data of Seki on completely crystalline poly(oxymethylene) were taken as the recommended data up to 300 K. This was made to join the heat capacity data of Hellwege, Knappe, and Wetzel on a highly crystalline sample to obtain the recommended values of heat capacities from 190 to 390 K. The recommended values of heat capacity of crystalline poly(oxymethylene) from 0 to 390 K are listed in table 4.

The heat capacity of crystalline poly(oxymethylene) at 390 K is 54.00 J $mol^{-1}K^{-1}$. If all the vibrations were fully excited, the heat capacity would be of the order of 99.7 J $mol^{-1}K^{-1}$ (12 R). Any type of extrapolation of the heat capacity from 390 K to the melting temperature is not justified because above 390 K an increase in the heat capacity is expected due to the excitation of the C–H bending vibrations. For this reason crystalline polyethylene [1] showed an upward trend from linearity in the temperature region close to the melting temperature.

Enthalpy, entropy, and Gibbs energy of crystalline poly(oxymethylene) were calculated by numerically integrating the heat capacity data. These thermodynamic functions are listed in table 4.

Table 2. Investigations not included in this study

Reference	Reason(s) for exclusion
Gray and Brenner (1965) [34]	Data reported on commercial samples of poly(oxymethylene) from 320 to 450K. Sample characterization not reported.
Slonimskii and Godovskii (1967) [41]	Data reported on uncharacterized sample of poly(oxypropylene) from 280 to 480K. A constant value of 106.5 J $mol^{-1}K^{-1}$ has been reported for molten poly(oxypropylene) from 350 to 480K.
Clegg, Gee, Melia and Tyson (1968) [17]	Data reported on poly(oxytetramethylene) $w^c = 0.6$. Their DSC data is 5% higher than adiabatic calorimetry data of references [16] and [18].
Doddi, Forsman and Price (1971) [43]	Data reported on poly[oxy(t-butyl) ethylene] in the glass transition and melting range only.
Bashirov, et. al. (1975, 1976) [44, 45]	Data reported on poly(oxymethylene). Sample characterization not reported. Data could not be retrieved from too small graphs.
Dröscher (1977) [42]	Data reported on completely crystalline copolymers of poly(oxymethylene) and poly(oxymethyleneoxyethylene). Heat capacity has been represented by the equation $C_p = 36.75 + 0.1425(T-298) + 80x_2$ J $mol^{-1}K^{-1}$ in the temperature range of 300 to 410K and at mole fractions of oxyethylene units $x_2 < 0.16$. Their data is 4-10% lower than the values reported here.

Table 3. Heat capacity measurements of poly(oxymethylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Hellwege, Knappe and Wetzel (1962) 32	1. Commercial sample: Delrin NC (DuPont)	310-410	Adiabatic (1%)	Graph
Dainton, Evans, Hoare and Melia (1962) 33	2. Commercial sample: Trioxane copolymer Highly crystalline	22-300	Adiabatic (1%)	Table
	3. Commercial sample: Delrin B-5522 (DuPont) MW = 45,000	22-300	Adiabatic (0.5%)	Table
Nakatsuka, Suga and Seki (1969) 35	7. Solid state polymerized $w^c \approx 1.0$	12-305	Adiabatic (15)	12-25K: Equation[a] 30-300 K: Graph
Wilski (1971) 36	8. Commercial sample: Hostaform C 9020 Contains 2% ethylene oxide $M_w = 58,000$ $\Delta H_f = 5.75$ kJ mol^{-1} $\rho = 1.413$ Mg m^{-3} $w^c = 0.57$	210-350	Adiabatic (Unreported)	Graph
Salinger (1974) [37]	9. Commercial sample: Delrin (DuPont)	0.4-4.0	Heat pulse (10%)	Table
White, Smith and Birch (1976) [38]	10. Single crystals texture (unknown crystallinity)	2-18	Heat pulse (5%)	2-10K: Equation[b] 12-18K: Table

[a] $C_p = 6.114 \cdot 10^{-4}T + 1.211 \cdot 10^{-5}T^2 - 7.95 \cdot 10^{-9}T^3$ J g^{-1}K^{-1}

[b] $C_p = 13.0 \pm 0.5$ μJ g^{-1}

Table 4. Recommended thermodynamic data of crystalline poly(oxymethylene)^a

T(K)	C_p ($J\ mol^{-1}K^{-1}$)	$H_T^c-H_o^c$ ($J\ mol^{-1}$)	S_T^c ($J\ mol^{-1}K^{-1}$)	$-(G_T^c-H_o^c)$ ($J\ mol^{-1}$)
0.0	0.0	0.0	0.0	0.0
0.1	0.0000077	0.00000045	0.0000065	0.00000019
0.2	0.0000113	0.0000013	0.0000125	0.0000012
0.3	0.0000201	0.0000029	0.0000186	0.0000027
0.4	0.0000345	0.0000056	0.0000262	0.0000049
0.5	0.0000561	0.0000100	0.0000361	0.0000080
0.6	0.0000866	0.0000170	0.0000489	0.0000122
0.7	0.000128	0.0000277	0.0000652	0.0000179
0.8	0.000182	0.0000430	0.0000856	0.0000254
0.9	0.000252	0.0000647	0.000111	0.0000352
1.0	0.000339	0.0000940	0.000142	0.0000478
1.2	0.000577	0.000184	0.000223	0.0000838
1.4	0.000917	0.000332	0.000336	0.000139
1.6	0.001381	0.000559	0.000488	0.000221
1.8	0.00199	0.000894	0.000684	0.000337
2.0	0.00278	0.00137	0.000933	0.000498
3.0	0.01014	0.00729	0.00323	0.00242
4.0	0.02551	0.02431	0.00803	0.00780
5.0	0.05178	0.06194	0.01631	0.01964
6.0	0.09146	0.1323	0.02904	0.04191
7.0	0.1466	0.2500	0.04707	0.07949
8.0	0.2186	0.4311	0.07115	0.1381
9.0	0.3086	0.6932	0.1019	0.2240
10.0	0.4172	1.055	0.1399	0.3442
12.0	0.6907	2.150	0.2390	0.7179
14.0	1.037	3.866	0.3706	1.322
16.0	1.452	6.345	0.5355	2.222

Table 4. Recommended thermodynamic data of crystalline poly(oxymethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1})
18.0	1.928	9.716	0.7334	3.486
20.0	2.455	14.09	0.9634	5.178
25.0	3.940	29.99	1.667	11.68
30.0	5.407	53.43	2.517	22.10
40.0	7.974	120.7	4.436	56.71
50.0	10.10	211.4	6.451	111.1
60.0	11.85	321.4	8.452	185.7
70.0	13.30	447.4	10.39	279.9
80.0	14.54	586.7	12.25	393.2
90.0	15.65	737.8	14.03	524.6
100.0	16.68	899.4	15.73	673.5
110.0	17.68	1071.	17.37	839.0
120.0	18.68	1253.	18.95	1021.
130.0	19.71	1445.	20.48	1218.
140.0	20.75	1647.	21.98	1430.
150.0	21.82	1860.	23.45	1657.
160.0	22.89	2084.	24.89	1899.
170.0	23.97	2318.	26.31	2155.
180.0	25.05	2563.	27.71	2425.
190.0	26.11	2819.	29.10	2709.
200.0	27.15	3085.	30.46	3007.
210.0	28.18	3362.	31.81	3318.
220.0	29.20	3649.	33.15	3643.
230.0	30.21	3946.	34.47	3981.
240.0	31.24	4253.	35.77	4333.
250.0	32.29	4571.	37.07	4697.

Table 4. Recommended thermodynamic data of crystalline poly(oxymethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1}K^{-1})
260.0	33.39	4899.	38.36	5074.
270.0	34.55	5239.	39.64	5464.
273.15	34.94	5348.	40.04	5589.
280.0	35.79	5590.	40.92	5867.
290.0	37.11	5955.	42.20	6282.
298.15	38.26	6262.	43.24	6630.
300.0	38.52	6333.	43.48	6711.
310.0	40.02	6725.	44.77	7152.
320.0	41.61	7134.	46.06	7606.
330.0	43.27	7558.	47.37	8073.
340.0	45.00	7999.	48.68	8553.
350.0	46.77	8458.	50.01	9047.
360.0	48.57	8935.	51.36	9554.
370.0	50.38	9430.	52.71	10073.
380.0	52.20	9942.	54.08	10607.
390.0	54.00	10473.	55.46	11155.

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[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 5. Heat capacity measurements of poly(oxyethylene)

Investigator	Sample no., characterication	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Beaumont, et al. (1966) [26]	11. Commercial sample: (Union Carbide) $\bar{M}$ =19,000 ΔH_f=8.20 kJ mol^{-1} w^c=0.95	90-360	Adiabatic (1%)	Table
	37. Commercial sample: (Shell Chemical Co.) $\bar{M}$ =670 ΔH_f=7.28 kJ mol^{-1} w^c=0.84	90-360	Adiabatic (1%)	Table^a
	38. Commercial sample: (Shell Chemical Co.) $\bar{M}$ =3,100 ΔH_f=8.50 kJ mol	90-360	Adiabatic (1%)	Table^a
Braun, Hellwege and Knappe (1967) [39]	12. Average data for eight different molten samples $\bar{M}_v$=1,000-2,900,000 ΔH_f=7.17-8.85 kJ mol^{-1} ρ=1.2019-1.2095 Mg m^{-3} w^c=0.76-0.91	310-370	Adiabatic (1%)	Equation^b

^{a}Data were interpolated using the spline function technique to give heat capacities at every ten degree interval.

$^b C_p$ = 0.497 + 2.37·10^{-4}(T-273) cal g^{-1}K^{-1}

2.3.2. Poly(oxyethylene)

Two investigations have been reported on the heat capacity of poly(oxyethylene) [26, 39]. Details of these investigations are given in table 5. The data which spans from 90 to 370 K are given in tables A3 and A4. These tables have been deposited with the Physics Auxiliary Service of the American Institute of Physics. All the solid samples studied were highly crystalline and vary in molecular weight from 670 to 19,000. The data on molten samples cover a broad range of molecular weight from 670 to 2,900,000.

Since the heat capacity of linear macromolecules from 90 K to the glass transition temperature has very limited or no dependence on crystallinity, the heat capacity from 90 to 220 K of sample 11 which has sufficiently high molecular weight and crystallinity ($w^c = 0.95$ and $\bar{M}_v = 19{,}000$) was taken to be the heat capacity of crystalline poly(oxyethylene). These values are listed in table 6.

The heat capacity of crystalline poly(oxyethylene) from 0 to 80 K was estimated by adding the heat capacities of crystalline polyethylene and crystalline poly(oxymethylene). This estimation is supported by observation that the heat capacity was found to be additive from 90 to 120 K within 3%. Further details about additivity of $-CH_2-$ and $-O-$ groups are given in section 3.

The heat capacity of crystalline poly(oxyethylene) between the glass transition temperature (232 K) and the melting temperature (342 K) was determined by linear extrapolation of the heat capacity data below the glass transition temperature. This linear extrapolation is supported by the observation that the sum of the heat capacities of crystalline poly(oxymethylene) and crystalline polyethylene from 230 to 340 K is quite linear. The heat capacity data on sample 11 from 160 to 220 K were curve fitted into the equation

$$C_p = 0.135T + 14.857 \text{ J mol}^{-1}\text{K}^{-1}. \quad (2)$$

The RMS deviation was 0.2%. Equation (2) was used to calculate the heat capacity of crystalline poly(oxyethylene) from 220 K to the melting temperature. These values are listed in table 6.

The recommended data on the heat capacity of molten poly(oxyethylene) were determined by curve fitting the data on samples 11, 12, 37, and 38 from 330 to 370 into the equation

$$C_p = 4.5362\cdot 10^{-2}T + 78.5 \text{ J mol}^{-1}\text{K}^{-1}. \quad (3)$$

The data by Braun, Hellwege, and Knappe [39] which are an average of eight samples of molecular weight ranging from 1,000 to 2,900,000 was given a weight factor of eight. The RMS deviation was 1.5%. Equation (3) was used to evaluate the heat capacity of molten poly(oxyethylene) from 232 to 370 K. These values are listed in table 7.

Enthalpy, entropy and Gibbs energy of crystalline and molten poly(oxyethylene) were calculated from 0 to 370 K by numerically integrating the heat capacity data. These thermodynamic functions are listed in tables 6 and 7.

Table 6. Recommended thermodynamic data of crystalline poly(oxyethylene)[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1})
0.0	0.0	0.0	0.0	0.0
10.0	(0.5137)[b]	1.605	0.1926	0.3211
20.0	(3.184)	20.09	1.245	4.816
30.0	(7.245)	72.24	3.249	25.23
40.0	(11.16)	164.3	5.851	69.80
50.0	(14.62)	293.2	8.708	142.3
60.0	(17.60)	454.3	11.64	244.0
70.0	(20.13)	642.9	14.54	375.0
80.0	(22.33)	855.2	17.38	534.8
90.0	24.90	1091.	20.15	723.4
100.0	26.93	1351.	22.88	938.6
110.0	28.78	1629.	25.54	1180.
120.0	30.44	1925.	28.12	1449.
130.0	32.10	2238.	30.62	1742.
140.0	33.57	2566.	33.05	2061.
150.0	35.05	2909.	35.42	2404.
160.0	36.53	3267.	37.73	2769.
170.0	37.82	3639.	39.98	3158.
180.0	39.11	4024.	42.18	3569.
190.0	40.40	4421.	44.33	4002.
200.0	41.88	4833.	46.44	4456.
210.0	43.17	5258.	48.52	4931.
220.0	44.64	5697.	50.56	5426.
230.0	(45.91)[c]	6149.	52.57	5942.
232.0(T_g)	(46.18)	6241.	52.97	6047.
240.0	(47.26)	6615.	54.55	6478.
250.0	(48.61)	7094.	56.51	7033.

Table 6. Recommended thermodynamic data of crystalline poly(oxyethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1})
260.0	(49.96)	7587.	58.44	7608.
270.0	(51.31)	8094.	60.35	8202.
273.15	(51.74)	8258.	60.96	8396.
280.0	(52.66)	8613.	62.24	8815.
290.0	(54.01)	9147.	64.11	9446.
298.15	(55.11)	9594.	65.64	9978.
300.0	(55.36)	9694.	65.97	10097.
310.0	(56.71)	10254.	67.81	10766.
320.0	(58.06)	10828.	69.63	11453.
330.0	(59.41)	11415.	71.43	12158.
340.0	(60.76)	12016.	73.23	12882.
342.0(T_m)	(61.03)	12138.	73.58	13028.

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b] Values estimated from additivity (10-80 K)

[c] Values estimated by linear extrapolation (230-342 K)

Table 7. Recommended Thermodynamic data of molten poly(oxyethylene)[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a - H_o^c$ (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	$-(G_T^a - H_o^c)$ (J mol^{-1})
232.0(T_g)	89.02	10731.	63.44	3988.
240.0	89.39	11445.	66.47	4508.
250.0	89.84	12341.	70.13	5191.
260.0	90.29	13241.	73.66	5910.
270.0	90.75	14147.	77.07	6663.
273.15	90.89	14437.	78.14	6912.
280.0	91.20	15056.	80.38	7451.
290.0	91.65	15971.	83.59	8271.
298.15	92.03	16724.	86.15	8967.
300.0	92.11	16890.	86.71	9122.
310.0	92.56	17813.	89.73	10005.
320.0	93.02	18741.	92.68	10917.
330.0	93.47	19673.	95.55	11858.
340.0	93.92	20610.	93.35	12827.
342.0(T_m)	94.01	20798.	98.90	13028.
350.0	94.38	21552.	101.1	13825.
360.0	94.83	22498.	103.7	14849.
370.0	95.28	23448.	106.3	15899.

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 8. Heat capacity measurements of poly(oxytrimethylene)

Investigator	Sample no. characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Yoshida, Sakiyama and Seki (1970) [15]	13. Quenched from 310 K to 80 K. Broad MWD $\bar{M}_n$=6,000 $w^c \approx 0$	90-210	Adiabatic (1%)	Table[a]
	14. Annealed at 260 K for 60 h. Broad MWD $\bar{M}_n$=6,000 w^c=0.73	90-310	Adiabatic (1%)	Table[a]
Yoshida, Suga and Seki (1973) [40]	15. Annealed at 273 K for 72 h and cooled to 80K at 5 deg h^{-1} $\bar{M}_w$=20,000 $\bar{M}_n$=11,000 w^c=0.67	1.4-20 13-330	Isoperibol Calorimeter Adiabatic (1%)	1.4-30:Equation[b] 40-330:Table[a]
	16. Annealed at 325 K for 1 h and cooled to 80K at 20 deg min^{-1} $\bar{M}_w$=20,000 $\bar{M}_n$=11,000 w^c=0.1	1.6-20 13-210	Isoperibol calorimeter Adiabatic (1%)	1.6-30:Equation[c] 40-330:Table[a]
	17. Cryst. at 215K from supercooled liquid $\bar{M}_w$=20,000 $\bar{M}_n$=11,000 w^c=0.41	13-65	Adiabatic (1%)	Table[a]

[a] Data were interpolated using spline function technique to give heat capacities at every ten degree interval.

[b] Author's tabulated data were curve fitted into the equation $C_p = \exp[-0.107976(\ln T)^3 + 0.229085(\ln T)^2 + 3.26828(\ln T) - 7.26364]$ J mol^{-1}K^{-1} (RMS deviation = 1.5%)

[c] Author's tabulated data were curve fitted into the equation $C_p = \exp[-0.147209(\ln T)^3 + 0.3586(\ln T)^2 + 3.11554(\ln T) - 6.74338]$ J mol^{-1}K^{-1} (RMS deviation = 6.9%).

2.3.3. Poly(oxytrimethylene)

Two investigations [15, 40] have been reported in the literature on the heat capacity of poly(oxytrimethylene). Details of these investigations are given in table 8. Heat capacities of five samples of crystallinity 0 to 0.73 have been measured over the temperature range of 1.4 to 330 K. The data on these samples are given in table A5. Table A5 has been deposited with the Physics Auxiliary Service of the American Institute of Physics. Low temperature heat capacity data on samples 15 and 16 were smoothed by curve fitting into a logarithmic function. These equations are listed in table 8.

To determine the heat capacity of completely crystalline and completely amorphous poly(oxytrimethylene), referred to hereafter as crystalline and amorphous poly(oxytrimethylene), the data at each temperature from 1.6 to 190 K were plotted as a function of crystallinity (w^c) and curve fitted into the two phase model equation

$$C_p = w^c C_p{}^c + (1 - w^c) C_p{}^a \tag{4}$$

where $C_p{}^c$ and $C_p{}^a$ are the heat capacity of crystalline and amorphous poly(oxytrimethylene). Plots of w^c vs C_p at several temperatures are given in figure 1. The results of crystallinity extrapolations to obtain heat capacity of crystalline and amorphous poly(oxytrimethylene) are given in table 9.

The heat capacity of amorphous poly(oxytrimethylene) obtained from crystallinity extrapolations was further smoothed as follows: heat capacity values from 16 to 30 K were curve fitted into the equation

$$C_p = \exp[-0.104273(\ln T)^3 + 0.129576 \times (\ln T)^2 + 3.45949(\ln T) - 6.81328] \text{J mol}^{-1}\text{K}^{-1}. \tag{5}$$

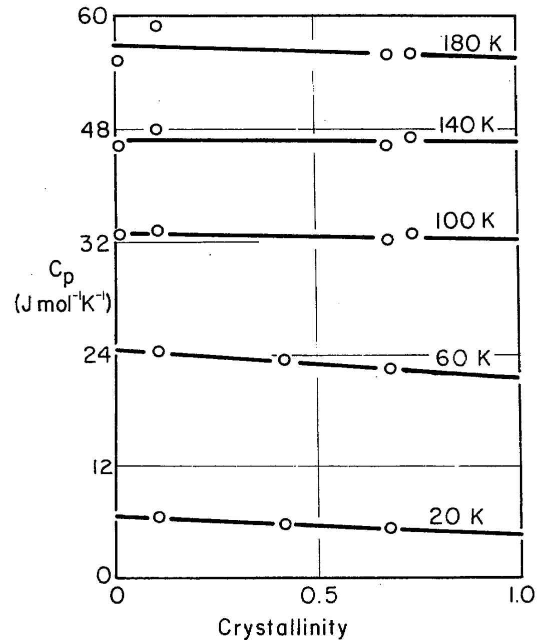

Figure 1. Heat capacity of poly(oxytrimethylene) as a function of crystallinity at various temperatures.

Table 9. Heat capacity vs. crystallinity: Results of curve fitting data into the equation $C_p = A\ w^c + B$

T(K)	C_p (crystalline) A+B (J mol^{-1} K^{-1})	C_p (amorphous) B (J mol^{-1}K^{-1})	RMS deviation (%)
1.6	0.002200	0.005793	
1.8	0.003318	0.008611	
2.0	0.004785	0.01231	
3.0	0.01929	0.04877	
4.0	0.05061	0.1268	
5.0	0.1049	0.2586	
6.0	0.1874	0.4510	
7.0	0.3020	0.7056	
8.0	0.4516	1.020	
9.0	0.6381	1.387	
10.0	0.8607	1.801	

Table 9. Heat capacity vs. crystallinity: Results of curve fitting data into the equation $C_p = A\, w^c + B$--Continued

T(K)	C_p (crystalline) A+B ($\mathrm{J\ mol^{-1}K^{-1}}$)	C_p (amorphous) B ($\mathrm{J\ mol^{-1}K^{-1}}$)	RMS deviation (%)
12.0	1.420	2.727	
14.0	2.102	3.717	0.4
16.0	2.834	4.659	2.8
18.0	3.769	5.634	1.1
20.0	4.750	6.457	0.2
30.0	9.173	11.33	0.2
40.0	13.92	16.07	0.7
50.0	17.44	20.66	0.7
60.0	21.42	24.44	0.1
70.0	25.96	27.54	
80.0	29.38	30.78	
90.0	33.41	34.45	2.1
100.0	36.08	36.78	0.9
110.0	38.08	39.64	0.3
120.0	40.47	42.50	0.3
130.0	42.66	44.67	1.0
140.0	46.41	46.68	1.5
150.0	48.52	49.47	1.3
160.0	50.87	52.05	1.1
170.0	52.58	54.84	1.3
180.0	55.37	56.91	2.2
190.0	56.63	63.74	1.8

Equation (5) fits the data from 1.6 to 20 K with a RMS deviation of 1.8%. The data from 10 to 50 K were curve fitted into the equation

$$C_p = \exp[0.111052(\ln T)^3 - 1.37813(\ln T)^2 + 6.79203(\ln T) - 9.09986]\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (6)$$

The RMS deviation was less than 0.1%. The data from 50 to 180 K were curve fitted into the equation

$$C_p = \exp[0.069093(\ln T)^3 - 1.02653(\ln T)^2 + 5.79383(\ln T) - 8.08411]\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (7)$$

The RMS deviation was 0.7%. To determine the recommended values of heat capacity at the temperatures close to the glass transition, the heat capacity data at 170, 180, and 190 K were curve fitted into the equation

$$C_p = 0.0238T^2 - 8.1232T + 747.944\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (8)$$

The smoothed values of the heat capacity of amorphous poly(oxytrimethylene) from eq (5), from 25 to 50 K, obtained from eq (6), and from 60 to 180 K, obtained from eq (7) are given in table 10. Heat capacities at 190 and 195 K were calculated using eq (8).

The heat capacity of crystalline poly(oxytrimethylene) obtained from crystallinity extrapolations was further smoothed as follows: Heat capacity values from 1.6 to 30 K were curve fitted into the equation

Table 10. Recommended thermodynamic data of amorphous poly(oxytrimethylene)[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a-H_0^a$ (J mol^{-1})	$S_T^a-S_0^a$ (J mol^{-1}K^{-1})	$H_T^a-H_0^c$ (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	$-(G_T^a-H_0^c)$ (J mol^{-1})
0.0	0.0	0.0	0.0	4007.	3.91	-4007.
1.0	0.001098	0.000155	0.000171	4007.	3.91	-4003
1.2	0.002072	0.000465	0.000451	4007.	3.91	-4002.
1.4	0.003556	0.001018	0.000874	4007.	3.91	-4001.
1.6	0.005684	0.001930	0.001480	4007.	3.91	-4000.
1.8	0.008593	0.003344	0.002309	4007.	3.91	-3999.
2.0	0.01242	0.005429	0.003404	4007.	3.91	-3999.
3.0	0.05003	0.03378	0.01439	4007.	3.92	-3995.
4.0	0.1292	0.1194	0.03848	4007.	3.95	-3991.
5.0	0.2605	0.3096	0.08038	4007.	3.99	-3987.
6.0	0.4498	0.6598	0.1437	4007.	4.05	-3983.
7.0	0.6979	1.229	0.2309	4008.	4.14	-3979.
8.0	1.003	2.075	0.3434	4009.	4.25	-3975.
9.0	1.359	3.251	0.4816	4010.	4.39	-3970.
10.0	1.761	4.808	0.645	4011.	4.55	-3966.
12.0	2.672	9.221	1.045	4016.	4.95	-3956.
14.0	3.676	15.56	1.531	4022.	5.44	-3946.
16.0	4.719	23.95	2.090	4030.	6.00	-3934.
18.0	5.755	34.43	2.706	4141.	6.62	-3922.

Table 10. Recommended thermodynamic data of amorphous poly(oxytrimethylene)[a]-Continued

T(K)	C_p (J mol^{-1}K^{-1})	H_T^a-H_o^a (J mol^{-1})	S_T^a-S_o^a (J mol^{-1}K^{-1})	H_T^a-H_o^c (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	-(G_T^a-H_o^c) (J mol^{-1})
20.0	6.749	46.94	3.364	4053.	7.27	-3908.
25.0	8.913	85.37	5.069	4092.	8.98	-3867.
30.0	11.34	136.0	6.909	4143.	10.82	-3818.
40.0	16.06	273.1	10.82	4280.	14.73	-3690.
50.0	20.67	456.8	14.90	4463.	18.81	-3523.
60.0	24.37	682.1	19.00	4689.	22.91	-3314.
70.0	27.80	943.2	23.02	4950.	26.93	-3065.
80.0	30.98	1237.	26.94	5244	30.85	-2776.
90.0	33.98	1556.	30.76	5569.	34.67	-2448.
100.0	36.82	1916.	34.49	5923.	38.40	-2083.
110.0	39.55	2298.	38.13	6305.	42.04	-1681.
120.0	42.18	2706.	41.68	6713.	45.59	-1242.
130.0	44.74	3141.	45.16	7148	49.07	- 769.4
140.0	47.24	3601.	48.57	7608.	52.48	- 261.7
150.0	49.69	4086.	51.91	8093.	55.82	- 279.8
160.0	52.10	4595.	55.20	8602.	59.10	854.5
170.0	54.49	5128.	58.43	9135.	62.33	1461.
180.0	56.86	5684.	61.61	9691.	65.52	2101.
190.0	63.74	6284.	64.85	10291.	68.76	2772.
195.0(T_g)	68.94	6616.	66.57	10622.	70.48	3120.
195.0	108.7	6616.	66.57	10622.	70.48	3120.
200.0	109.2	7161.	69.33	11167.	73.23	3479.
210.0	110.2	8258.	74.69	12264.	78.59	4238.
220.0	111.3	9366.	79.84	13372.	83.74	5050.
230.0	112.3	10484.	84.81	14490.	88.71	5913.
240.0	113.3	11611.	89.61	15617.	93.51	6824.
250.0	114.3	12749.	94.25	16755.	98.15	7782.

Table 10. Recommended thermodynamic data of amorphous poly(oxytrimethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	H_T^a-H_o^a (J mol^{-1})	S_T^a-S_o^a (J mol^{-1}K^{-1})	H_T^a-H_o^c (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	-(G_T^a-H_o^c) (J mol^{-1}K^{-1})
260.0	115.3	13897	98.75	17903.	102.7	8786.
270.0	116.3	15055.	103.1	19061.	107.0	9835.
273.15	116.6	15428.	104.5	19434.	108.4	10180.
280.0	117.3	16223.	107.4	20229.	111.3	10927.
290.0	118.3	17402.	111.5	21408.	115.4	12060.
298.15	119.2	18375.	114.8	22381.	118.7	13020.
300.0	119.3	18590.	115.5	22596.	119.4	13234.
308.0(T_m)	120.1	19548.	118.7	23554.	122.6	14203.
310.0	120.3	19788.	119.5	23794.	123.4	14449.
320.0	121.4	20997.	123.3	25003.	127.2	15701.
330.0	122.4	22216.	127.1	26221.	131.0	16992.

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

$$C_p = \exp[-0.10064(\ln T)^3 + 0.256868(\ln T)^2 + 3.20608(\ln T) - 7.66109]\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (9)$$

Equation (9) fits the data from 1.6 to 20 K with a RMS deviation of 1.0%. The data from 10 to 60 K were curve fitted into the equation

$$C_p = \exp[0.158106(\ln T)^3 - 2.08972(\ln T)^2 + 10.181(\ln T) - 14.4428]\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (10)$$

The RMS deviation was 1.1%. The data from 60 to 190 K were curve fitted into the equation

$$C_p = \exp[0.288418(\ln T)^3 - 4.25857(\ln T)^2 + 21.6604(\ln T) - 34.0241]\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (11)$$

The RMS deviation was 1.0%. The smoothed values of the heat capacity of crystalline poly(oxytrimethylene) from 1 to 20 K, obtained from eq (9), from 25 to 60 K, obtained from eq (10) and from 70 to 190 K, obtained from eq (11) are listed in table 11.

The heat capacity of crystalline poly(oxytrimethylene) between the glass transition temperature (195 K) and the melting temperature (308 K) was determined by linear extrapolation of the heat capacity data below the glass transition temperature. This linear extrapolation is supported by the observation that the sum of the heat capacities of crystalline polyethylene and crystalline poly(oxymethylene) from 190 to 310 K is quite linear. The crystallinity extrapolated heat capacity values of crystalline poly(oxytrimethylene) from 150 to 190 K were curve fitted into the equation

$$C_p = 0.2072\,T + 17.57\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (12)$$

The RMS deviation was 0.5%. Equation (12) was used to calculate the heat capacity of crystalline poly(oxytrimethylene) from 190 to the melting temperature. These values are listed in table 11.

The recommended data on the heat capacity of molten poly(oxytrimethylene) were determined by curve fitting the data

Table II. Recommended thermodynamic data of crystalline poly(oxytrimethylene)[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1})
0.0	0.0	0.0	0.0	0.0
1.0	0.000471	0.0000684	0.0000753	0.0000069
1.2	0.000851	0 000198	0.000192	0.0000329
1.4	0.001420	0.000421	0.000364	0.0000875
1.6	0.002225	0.000782	0.000603	0.000183
1.8	0.003318	0.001331	0.000925	0.000334
2.0	0.004753	0.002132	0.001346	0.000559
3.0	0.01902	0.01290	0.005519	0.003662
4.0	0.05024	0.04583	0.01478	0.01329
5.0	0.1048	0.1212	0.03136	0.03567
6.0	0.1881	0.2651	0.05737	0.07917
7.0	0.3038	0.5082	0.09462	0.1542
8.0	0.4545	0.8844	0.1446	0.2727
9.0	0.6414	1.429	0.2086	0.4481
10.0	0.8645	2.179	0.2874	0.6948
12.0	1.416	4.437	0.4917	1.463
14.0	2.094	7.927	0.7594	2.704
16.0	2.879	12.88	1.089	4.542
18.0	3.749	19.50	1.478	7.100
20.0	4.678	27.92	1.920	10.49
25.0	7.026	57.29	3.222	23.25
30.0	9.313	98.16	4.706	43.01
40.0	13.65	213.3	7.987	106.2
50.0	17.64	370.0	11.47	203.4
60.0	21.37	565.2	15.02	335.8
70.0	25.82	802.3	18.66	504.1

Table 11. Recommended thermodynamic data of crystalline poly(oxytrimethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1})
80.0	29.59	1079.	22.36	709.2
90.0	32.90	1392.	26.04	951.3
100.0	35.87	1736.	29.67	1229.
110.0	38.58	2109.	33.21	1544.
120.0	41.11	2507.	36.68	1893.
130.0	43.51	2930.	40.07	2277.
140.0	45.83	3377.	43.37	2694.
150.0	48.11	3847.	46.61	3144.
160.0	50.37	4339.	49.79	3627.
170.0	52.65	4854.	52.91	4140.
180.0	54.97	5392.	55.99	4685.
190.0	(57.33)[b]	5954	59.02	5260.
195.0(T_g)	(57.97)	6241.	60.52	5559.
200.0	(59.01)	6533.	62.00	5865.
210.0	(61.08)	7134.	64.93	6500.
220.0	(63.15)	7755.	67.82	7163.
230.0	(65.23)	8397.	70.67	7856.
240.0	(67.30)	9060.	73.49	8576.
250.0	(69.37)	9743.	76.28	9325.
260.0	(71.44)	10447.	79.04	10102.
270.0	(73.51)	11172.	81.77	10906.
273.15	(74.18)	11408.	82.64	11168.
280.0	(75.59)	11917.	84.48	11736.
290.0	(77.66)	12684.	87.17	12595.
298.15	(79.36)	13327.	89.36	13318.
300.0	(79.73	13470.	89.84	13480.

Table 11. Recommended thermodynamic data of crystalline poly(oxytrimethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_o^c$ (J mol^{-1})	S_T^c (J mol^{-1}K^{-1})	$-(G_T^c-H_o^c)$ (J mol^{-1})
308.0(T_m)	(81.39)	14115.	91.96	14203.

[a]The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b]Estimated by linear extrapolation (190-308K)

on samples 13 and 6 from 200 to 210 K and samples 14 and 15 from 300 to 330 K into the equation

$$C_p = 0.10094\,T + 89.055\ \text{J mol}^{-1}\text{K}^{-1}. \tag{13}$$

The RMS deviation was 2.5%. Equation (13) was used to evaluate the heat capacity of molten poly(oxytrimethylene) from 195 to 330 K. These values are listed in table 10.

Enthalpy, entropy, and Gibbs energy of crystalline and amorphous poly(oxytrimethylene) were calculated from 0 to 330 K by numerically integrating the heat capacity data. These thermodynamic functions are listed in tables 10 and 11.

2.3.4. Poly(oxytetramethylene)

Three investigations [16-18] have been reported in the literature on the heat capacity of poly(oxytetramethylene). Details of these investigations are given in table 12. Heat capacity of four samples of crystallinity from 0.5 to 0.6 have been measured over the temperature range of 5 to 340 K. The data on these samples are given in tables A6 and A7. These tables have been deposited with the Physics Auxiliary Service of the American Institute of Physics. Since the crystallinity range of the samples studied is very limited, the calculation of the heat capacity of crystalline and amorphous poly(oxytetramethylene) from crystallinity extrapolations using the two phase model was not attempted. Only the recommended data for the heat capacity of emicrystalline poly(oxytetramethylene) ($w^c \simeq 0.55$) from 0 K to he glass transition temperature (189 K) and of molten poly(oxyetramethylene) from 189 to 340 K have been derived.

The recommended data on the heat capacity of poly(oxytetramethylene) of crystallinity 0.55 from 0 to 160 K were determined by averaging the data of samples 19, 20, and 37 at each temperature. The heat capacity values at 170 to 180 K are somewhat higher, because they are associated with the beginning of the glass transition. The data at 170 and 180 K were determined by linearly extrapolating the data below 160 K. The heat capacity values from 130 to 160 K were curve fitted into the equation

$$C_p = 0.3325\,T + 14.67\ \text{J mol}^{-1}\text{K}^{-1}. \tag{14}$$

The RMS deviation was 0.1%. The recommended value of heat capacities by averaging the data from 0 to 160 K and from eq (14) from 170 K to 189 K are listed in table 13.

The recommended data on heat capacity of molten poly(oxytetramethylene) were determined by curve fitting the data on samples 19, 20, and 37 from 280 to 340 K into the equation

$$C_p = 0.17229T + 91.46\ \text{J mol}^{-1}\text{K}^{-1}. \tag{15}$$

The RMS deviation was 0.5%. Equation (15) was used to calculate the heat capacity of molten poly(oxytetramethylene) from 189 to 340 K. These values are listed in table 14.

2.3.5 Poly(oxyoctamethylene)

Only one investigation [20] has been reported in the literature which deals with the heat capacity of poly(oxyoctamethylene). Details of this investigation are given in table 15. Heat capacity of three samples have been measured over the temperature range of 14 to 360 K. The data on these samples are given in table 16. Solution grown sample 21, a mixture of orthorhombic polyethylene-like structure and monoclinic poly(oxytetramethylene)-like structure is highly crystalline ($w^c = 0.91$). Samples 22 and 23 are melt crystallized and contain the monoclinic modification only. Crystallinity of sample 22 is 0.73. The crystallinity of sample 23 is not reported.

Since the heat capacity measurements have been made on samples of different crystal modification and the crystallinity determination is incomplete, the data has not been further analyzed to determine the heat capacity of crystalline poly(octamethylene). The data on sample 21 ($w^c = 0.91$) can serve as a reasonable approximation to the heat capacity of crystalline poly(oxyoctamethylene).

2.3.6 Poly(oxymethyleneoxyethylene)

Only one investigation [23] has been reported in the literature which deals with the heat capacity of poly(oxymethyleneox-

Table 12. Heat capacity measurements of poly(oxytetramethylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Yoshida, Suga and Seki (1973) [16]	19. Annealed at 300K for 40 h. $\bar{M}$ =90,000 ΔH_f=8.68 kJ mol^{-1} w^c=0.60	12-330	Adiabatic (1%)	Table[a]
	20. Rapidly cooled to liquid nitrogen temperature. $\bar{M}$ =90,000 w^c=0.56	14-330	Adiabatic (1%)	Table[a]
Lebedev and Lityagov (1977) [18]	37. Anneal. at 290K for 48 h. $\bar{M}$ =430,000 ΔH_f=7.19 kJ mol^{-1} w^c=0.50	5-330	Adiabatic (0.2%)	Table, graph

[a] Data were interpolated using spline function technique to give heat capacities at every ten degree interval.

Table 13. Recommended heat capacity data for semi-crystalline poly(oxytetramethylene) below the glass transition (w^c=0.55±0.05)[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
0.0	0.0
5.0	0.1671
10.0	1.470
20.0	6.592
30.0	12.42
40.0	18.32
50.0	24.63
60.0	29.74
70.0	34.61
80.0	39.41
90.0	43.67
100.0	47.27
110.0	50.72
120.0	54.70
130.0	57.99
140.0	61.12
150.0	64.46
160.0	67.96
170.0	71.20
180.0	74.52
189.0(T_g)	77.51

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 14. Recommended heat capacity data for molten poly(oxytetramethylene)[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
189.0(T_g)	124.0
190.0	124.2
200.0	125.9
210.0	127.6
220.0	129.4
230.0	131.1
240.0	132.8
250.0	134.5
260.0	136.3
270.0	138.0
280.0	139.7
290.0	141.4
300.0	143.1
310.0	144.9
320.0	146.6
330.0(T_m)	148.3
340.0	150.0

[a] The tables may contain more significant figures than justified by both sources of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 15. Heat capacity measurements of poly(oxyoctamethylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Yoshida, Suga and Seki (1973) [20]	21. Soln. grown in methanol at 343 K $\bar{M}$=7,000 ΔH_f=26.6 kJ mol^{-1} w^c=0.91	13-360	Adiabatic (1%)	Table[a]
	22. Melt crystallized. Annealed at 300 K for 40 h. $\bar{M}$=7,000 ΔH_f=21.3 kJ mol^{-1}	13-360	Adiabatic (1%)	Table[a]
	23. Melt crystallized. Cooled to liq. nitrogen temp. at 18 deg min^{-1} $\bar{M}$=7,000	13-360	Adiabatic (1%)	Table[a]

[a] Data were interpolated using the spline function technique to give heat capacities at every ten degree interval.

Table 16. Heat capacity of various poly(oxyoctamethylene)s[a] in J $mol^{-1}K^{-1}$

T(K)	21	22	23
14	5.177	4.648	4.814
16	5.907	5.820	6.007
18	7.308	7.407	7.709
20	9.135	9.156	9.806
25	13.98	14.04	14.58
30	19.84	19.52	19.96
40	31.11	31.47	31.70
50	42.74	42.69	42.88
60	53.27	53.92	53.85
70	62.57	63.31	63.06
80	71.95	71.67	71.75
90	79.78	80.17	79.80
100	86.86	87.39	86.64
110	92.94	93.79	93.46
120	99.05	99.30	99.88
130	104.7	105.3	105.6
140	110.5	111.0	111.2
150	116.1	116.6	116.7
160	120.8	121.2	121.7
170	126.7	126.5	126.9
180	131.8	131.5	132.8
190	137.4	136.1	138.1
200	143.5	141.7	143.2
210	149.4	147.6	149.8
220	155.7	154.6	157.2
230	163.8	162.0	166.0
240		170.2	175.1

Table 16. Heat capacity of various poly(oxyoctamethylene)s[a] in J $mol^{-1}K^{-1}$ --Continued

T(K)	21	22	23
250	Glass Transition		
260	188.5		
270	194.7		211.9
280	203.0	219.9	216.3
290		227.0	
300		236.0	
	Melting		
350	283.9	283.9	283.9
360	285.7	285.7	285.7

[a] Sample numbers correspond to the samples described in table 22.

Table 17. Heat capacity measurement of poly(oxymethyleneoxyethylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Clegg and Melia (1969) [23]	27. Annealed at 320 K for 16 h. $\bar{M}_n$=2,800 ΔH_f=9.68 kJ mol^{-1} w^c=0.58	80-390	DSC, Adiabatic (Unreported)	Table

yethylene). Details of this investigation are given in table 17. The data which span from 80 to 390 K are given in table A8. Table A8 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Since the heat capacity of linear macromolecules from 100 K to the glass transition temperature have very limited or no dependence on crystallinity, the heat capacity from 100 to 200 K of sample 27 is a good approximation to the heat capacity of crystalline poly(oxymethyleneoxyethylene).

The heat capacity of crystalline poly(oxymethyleneoxyethylene) from 0 to 90 K was estimated by appropriately adding the heat capacity of crystalline polyethylene and crystalline poly(oxymethylene)

$$C_p\text{-poly(oxymethyleneoxyethylene)}$$
$$= C_p\text{-poly(ethylene)} + 2C_p\text{-poly(oxymethylene)}. \quad (16)$$

This estimation is supported by the observation that eq (16) holds for the experimental data of poly(oxymethyleneoxyethylene) from 110 to 140 K within 3% when one inserts the recommended data of crystalline poly(oxymethylene) (discussed in sec. 2.3.1) and the recommended data of crystalline polyethylene (discussed in ref. [1]). Further details about additivity of the heat capacity of $-CH_2-$ and $-O-$ groups are given in section 3.

The heat capacity of crystalline poly(oxymethyleneoxyethylene) between the glass transition temperature (209 K) and the melting temperature (328 K) was determined by linear extrapolations of the heat capacity data below the glass transition temperature. This linear extrapolation is supported by the observation that the sum of the heat capacities of crystalline poly(oxymethylene) and crystalline polyethylene from 200 to 340 K is quite linear. The heat capacity data on sample 27 from 150 to 200 K were curve fitted into the equation

$$C_p = 0.3007\,T + 9.71 \text{ J mol}^{-1}\text{K}^{-1}. \qquad (17)$$

The RMS deviation was 0.5%. Equation (17) was used to calculate the heat capacity of crystalline poly(oxymethyleneoxyethylene) from 209 to 328 K. These values are listed in table 18.

The recommended data on the heat capacity of molten poly(oxymethyleneoxyethylene) were determined by curve-fitting the data on sample 27 from 330 to 390 K into the equation

Table 18. Recommended thermodynamic data of crystalline poly(oxymethyleneoxyethylene)[a]

T(K)	C_p (J mol^{-1} K^{-1})	$H^c_T-H^c_o$ (J mol^{-1})	S^c_T (J mol^{-1} K^{-1})	$-(G^c_T-H^c_o)$ (J mol^{-1})
0	0	0	0	0
10.0	(0.9309)[b]	2.907	0.3487	0.5801
20.0	(5.639)	35.75	2.224	8.722
30.0	(12.65)	127.2	5.742	45.06
40.0	(19.14)	286.1	10.24	123.6
50.0	(24.72)	505.4	15.11	249.9
60.0	(29.45)	776.3	20.03	425.7
70.0	(33.43)	1090.	24.88	650.6
80.0	(36.87)	1442.	29.57	923.2
90.0	(39.96)	1826.	34.09	1242.
100.0	41.19	2232.	38.37	1605.
110.0	44.23	2659.	42.44	2009.
120.0	47.05	3116.	46.41	2454.
130.0	4979	3600.	50.29	2938.
140.0	52.53	4111.	54.08	3460.
150.0	55.12	4650.	57.79	4019.
160.0	57.86	5215.	61.44	4615.
170.0	60.61	5807.	65.03	5248.
180.0	63.50	6427.	68.58	5916.
190.0	66.53	7078.	72.09	6619.

Table 18. Recommended thermodynamic data of crystalline poly(oxymethyleneoxyethylene)[a]--Continued

T(K)	C_p (J mol^{-1} K^{-1})	$H_T^c-H_0^c$ (J mol^{-1})	S_T^c (J mol^{-1} K^{-1})	$-(G_T^c-H_0^c)$ (J mol^{-1})
200.0	70.39	7762.	75.60	7358.
209.0(T_g)	(72.56)[c]	8403.	78.73	8053
210.0	(72.86)	8476.	79.08	8131.
220.0	(75.86)	9219.	82.54	8940.
230.0	(78.87)	9993.	85.98	9782.
240.0	(81.88)	10797.	89.40	10659.
250.0	(84.89)	11630.	92.80	11570.
260.0	(87.89)	12494.	96.19	12515.
270.0	(90.90)	13388.	99.56	13494.
273.15	(91.86)	13681.	100.6	13814.
280.0	(93.91)	14312.	102.9	14506.
290.0	(96.91)	15266.	106.3	15552.
298.15	(99.38)	16071.	109.0	16435.
300.0	(99.92)	15251.	109.6	16632.
310.0	(102.9)	17265.	112.9	17744.
320.0	(105.9)	18309.	116.3	18890.
328.0(T_m)	(108.3)	19166.	118.9	19831.

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[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b] Value estimated from additivity (10-90 K)

[c] Values estimated by linear extrapolation (209-328 K)

$$C_p = 0.1106T + 102.89 \text{ J mol}^{-1}\text{K}^{-1}. \quad (18)$$

The RMS deviation less than 0.1%. Equation (18) was used to evaluate the heat capacity of molten poly(oxymethyleneoxyethylene) from 209 to 390 K. These values are listed in table 19.

Enthalpy, entropy, and Gibbs energy of crystalline and molten poly(oxymethyleneoxyethylene) were calculated from 0 to 328 K by numerically integrating the heat capacity data. These thermodynamic functions are listed in tables 18 and 19.

2.3.7. Poly(oxymethyleneoxytetramethylene)

Only one investigation [24] has been reported in the literature which deals with the heat capacity of poly(oxymethyleneoxytetramethylene). Details of this investigation are given in table 20. The data which span from 80 to 360 K are given in table A9. Table A9 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Since the heat capacity of linear macromolecules from 100 K to the glass transition temperature has very limited or no dependence on crystallinity, the heat capacity from 100 to 180 K of sample 28 is a good approximation to the heat capacity of crystalline poly(oxymethyleneoxytetramethylene).

The heat capacity of crystalline poly(oxymethyleneoxytetramethylene) from 0 to 90 K was estimated by appropriately adding the heat capacity of crystalline polyethylene and crystalline poly(oxymethylene)

$$C_p\text{-poly(oxymethyleneoxytetramethylene)} = 3C_p\text{-polyethylene} + 2C_p\text{-poly(oxymethylene)}. \quad (19)$$

This estimation is supported by the observation that eq (19) holds for the experimental data of poly(oxymethyleneoxytetramethylene) from 100 to 150 K within 2% on insertion of the recommended data of crystalline poly(oxymethylene) (discussed in sec. 2.3.1) and of the recommended data of crystalline polyethylene (discussed in ref. [1]). Further details about the additivity of the heat capacity of $-CH_2-$ and $-O-$ groups are given in section 3.

Table 19. Recommended thermodynamic data of molten poly(oxymethyleneoxyethylene)[a]

T(K)	C_p (J mol^{-1} K^{-1})	$H_T^a-H_o^c$ (J mol^{-1})	S_T^a (J mol^{-1} K^{-1})	$-(G_T^a-H_o^c)$ (J mol^{-1})
209.0(T_g)	126.0	20089.	110.3	2957.
210.0	126.1	20215.	110.9	3067.
220.0	127.2	21481.	116.8	4206.
230.0	128.3	22759.	122.4	5402.
240.0	129.4	24048.	127.9	6654.
250.0	130.5	25348.	133.2	7960.
260.0	131.6	26659.	138.4	9318.
270.0	132.8	27981.	143.4	10726.
273.15	133.1	28406.	144.9	11188.
280.0	133.9	29314.	148.2	12184.
290.0	135.0	30658.	152.9	13690.
298.15	135.9	31768.	156.7	14960.
300.0	136.1	32013.	157.5	15242.
310.0	137.2	33379.	162.0	16840.
320.0	138.3	34757.	166.4	18482.
328.0(T_m)	139.2	35866.	169.8	19831.
330.0	139.4	36145.	170.6	20167.
340.0	140.5	37544.	174.8	21895.
350.0	141.6	38955.	178.9	23663.
360.0	142.7	40376.	182.9	25473.
370.0	143.8	41809.	186.8	27321.
380.0	144.9	43253.	190.7	29209.
390.0	146.0	44707.	194.5	31135.

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 20. Heat capacity measurement of poly(oxymethyleneoxytetramethylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Clegg and Melia (1970) [24]	28. Annealed at 320 K for 24 h. $\bar{M}_n$=72,000 ΔH_f=7.17 kJ mol^{-1} w^c=0.50	80-360	DSC, Adiabatic (Unreported)	Table

The heat capacity of crystalline poly(oxymethyleneoxytetramethylene) between the glass transition temperature (189 K) and the melting temperature (296 K) was determined by linear extrapolation of the heat capacity data below the glass transition temperature. This linear extrapolation is supported by the observation that the sum of the heat capacity of crystalline poly(oxymethylene) and crystalline polyethylene from 190 to 300 K is quite linear. The heat capacity data on sample 28 from 140 to 180 K were curve fitted into the equation

Table 21. Recommended thermodynamic data of crystalline poly(oxymethyleneoxytetramethylene)^a

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^c-H_0^c$ (J mol^{-1})	S_T^c (J mol^{-1} K^{-1})	$-(G_T^c-H_0^c)$ (J mol^{-1})
0.0	0.0	0.0	0.0	0.0
10.0	(1.124)^a	3.515	0.4219	0.7050
20.0	(7.098)	44.63	2.758	10.54
30.0	(16.33)	161.8	7.255	55.87
40.0	(25.51)	371.0	13.17	155.6
50.0	(33.77)	667.4	19.73	319.2
60.0	(40.94)	1041.	26.52	550.3
70.0	(47.09)	1481.	33.29	849.6
80.0	(52.45)	1979.	39.94	1216.
90.0	(57.27)	2527.	46.40	1648.
100.0	60.47	3116.	52.60	2144.
110.0	65.27	3745.	58.59	2700.
120.0	70.07	4421.	64.48	3316.
130.0	74.77	5146.	70.27	3990.
140.0	79.36	5916.	75.98	4721.
150.0	83.76	6732.	81.61	5510.
160.0	87.94	7590.	87.15	6354.

Table 21. Recommended thermodynamic data of crystalline poly(oxymethyleneoxytetramethylene)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H^c_T-H^c_o$ (J mol^{-1})	S^c_T (J mol^{-1}K^{-1})	$-(G^c_T-H^c_o)$ (J mol^{-1})
170.0	92.44	8492.	92.62	7253.
180.0	97.03	9440.	98.03	8206.
189.0(T_g)	(100.9)[b]	10330.	102.9	9109.
190.0	(101.3)	10431.	103.4	9213.
200.0	(105.7)	11466.	108.7	10273.
210.0	(110.1)	12545.	114.0	11386.
220.0	(114.5)	13668.	119.2	12552.
230.0	(118.9)	14836.	124.4	13770.
240.0	(123.3)	16047.	129.5	15039.
250.0	(127.7)	17302.	134.6	16360.
260.0	(132.1)	18601.	139.7	17732.
270.0	(136.5)	19944.	144.8	19155.
273.15	(137.9)	20377.	146.4	19614.
280.0	(140.9)	21332.	149.9	20628.
290.0	(145.3)	22763.	154.9	22152.
296.0(T_m)	(148.0)	23643.	157.9	23090.

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b] Values estimated from additivity (10-90 K).

[c] Values estimated by linear extrapolation (189-296 K).

Table 22. Recommended thermodynamic data of molten poly(oxymethyleneoxytetramethylene)[a]

T(K)	C_p (J mol^{-1}K^{-1})	H^a_T-H^c_0 (J mol^{-1})	S^a_T (J mol^{-1}K^{-1})	-(G^a_T-H^c_0) (J mol^{-1})
189.0(T_g)	174.8	18247.	123.9	5168.
190.0	175.0	18422.	124.8	5293.
200.0	176.8	20181.	133.8	6586.
210.0	178.5	21958.	142.5	7968.
220.0	180.3	23752.	150.9	9435.
230.0	182.1	25564.	158.9	10984.
240.0	183.9	27394.	166.7	12612.
250.0	185.7	29242.	174.2	14317.
260.0	187.5	31108.	181.6	16096.
270.0	189.3	32992.	188.7	17948.
273.15	189.8	33598.	190.9	18555.
280.0	191.0	34893	195.6	19869.
290.0	192.8	36813.	202.3	21859.
296.0(T_m)	193.9	37973.	206.3	23090.
298.5	194.3	38400.	207.7	23540
300.0	194.6	38750.	208.9	23915.
310.0	196.4	40705.	215.3	26036.
320.0	198.2	42678.	221.6	28220.
330.0	200.0	44669.	227.7	30466.
340.0	201.8	46678.	233.7	32773.
350.0	203.6	48704.	239.6	35140.
360.0	205.3	50749.	245.3	37564.

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

$$C_p = 0.4402T + 17.67 \text{ J mol}^{-1}\text{K}^{-1}. \quad (20)$$

The RMS deviation was 0.1%. Equation (20) was used to calculate the heat capacity of crystalline poly(oxymethyleneoxytetramethylene) from 189 to 296 K. These values are listed in table 21.

The recommended data on the heat capacity of molten poly(oxymethyleneoxyethylene) were determined by curve fitting the data on sample 28 from 300 to 360 K into the equation

$$C_p = 0.1786T + 141.04 \text{ J mol}^{-1}\text{K}^{-1}. \quad (21)$$

The RMS deviation was less than 0.1%. Equation (21) was used to evaluate the heat capacity of molten poly(oxymethyleneoxytetramethylene) from 189 to 360 K. These values are listed in table 22.

Enthalpy, entropy, and Gibbs energy of crystalline and molten poly(oxymethyleneoxytetramethylene) were calculated from 0 to 296 K by numerically integrating the heat capacity data. These thermodynamic functions are list in tables 21 and 22.

2.3.8 Poly(oxypropylene)

Only one investigation [26] has been reported in the literature which deals with the heat capacity of poly(oxypropylene). Details of this investigation are given in table 23. The heat capacity of largely atactic amorphous and semicrystalline ($w^c = 0.25$) samples have been measured from 80 to 360 K.

The heat capacity of both the samples below the glass transition temperature has been represented by the equation

$$C_p = -3.899 \cdot 10^{-4}\, T^{-2} + 0.7382\, T + 3.451 \text{ J mol}^{-1}\text{K}^{-1}. \quad (22)$$

Heat capacity of molten poly(oxypropylene) has been represented by the equation

$$C_p = 0.1577T + 63.92 \text{ J mol}^{-1}\text{K}^{-1}. \quad (23)$$

The recommended heat capacity data for poly(oxypropylene) below the glass transition, which are independent of the crystallinity, obtained from eq (22) are listed in table 24. The recommended values for molten poly(oxypropylene) obtained from eq (23) are listed in table 25.

2.3.9. Poly(oxy-1,4-phenylene)

Only one investigation [29] has been reported in the literature which deals with the heat capacity of poly(oxy-1,4-phenylene). Details of this investigation are given in table 26. Heat capacity of an amorphous sample and a semicrystalline sample ($w^c = 0.72$) have been measured over the temperature range of 300 to 620 K. The amorphous sample crystallizes above the glass transition at 375 K. The data on these samples are given in

Table 23. Heat capacity of poly(oxypropylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Beaumont, et al. (1966) [26]	24. Amorphous	80-360	Adiabatic (1%)	80-190 K:Equation[a] 200-360 K:Equation[b]
	25. Ppt. from methanol soln. $\bar{M}_v$=1,000,000 ρ=1.041 Mg m^{-3} w^c=0.25	80-370	Adiabatic (1%)	80-190 K:Equation[a] 200-270 K:Graph 340-370 K:Equation[b]

[a] $C_p = 0.0142 + 1.556\cdot10^{-3}T - 1.604\cdot10^{-6}T^2$ cal g^{-1}K^{-1}

[b] $C_p = 0.236 + 6.5\cdot10^{-4}T$ cal g^{-1}K^{-1}

Table 24. Recommended heat capacity data for poly(oxypropylene) below the glass transition[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
80.0	31.21
90.0	34.33
100.0	37.37
110.0	40.33
120.0	43.22
130.0	46.03
140.0	48.76
150.0	51.41
160.0	53.98
170.0	56.48
180.0	58.89
190.0	61.23
198.0(T_g)	63.05

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

table A10. Table A10 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Below the glass transition temperature, the heat capacity of amorphous and semicrystalline samples are in good agreement. Thus the heat capacity of poly(oxy-1,4-phenylene) below the glass transition was curve fitted into the equation

$$C_p = 0.337T + 7.95 \text{ J mol}^{-1}\text{K}^{-1}. \qquad (24)$$

The RMS deviation was 1.2%. Equation (24) was used to calculate the heat capacity of poly(oxy-1,4-phenylene) from 300 to 358 K. These values are listed in table 27.

Amorphous poly(oxy-1,4-phenylene) crystallizes above the glass transition temperature. Thus the heat capacity data on the

Table 25. Recommended heat capacity data for molten poly(oxypropylene)[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
198.0(T_g)	95.20
200.0	95.46
210.0	97.04
220.0	98.61
230.0	100.2
240.0	101.8
250.0	103.4
260.0	105.0
270.0	106.6
273.15	107.1
280.0	108.2
290.0	109.7
298.15	111.0
300.0	111.3
310.0	112.9
320.0	114.5
330.0	116.1
340.0	117.6
348.0(T_m)	118.9
350.0	119.2
360.0	120.8
370.0	122.3

[a] The tables may contain more significant figures than justified by both sources of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 26. Heat capacity measurements of poly(oxy-1,4-phenylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Wrasidlo (1972) [29]	29. Quenched from the melt w^c=0 Cryst. at 300 K to give a semi-crystalline sample ΔH_f=5.23 kJ mol^{-1} w^c=0.70 (X-ray)	300-620	DSC (3%)[a]	Graph
	30. Cold cryst. at 500 K ΔH_f=5.64 kJ mol^{-1} w^c=0.72 (X-ray)	300-620	DSC (3%)[a]	Graph

[a] Data reported in the form of small graphs. Error in data retrieval increases the uncertainty to 5%.

amorphous sample above the glass transition and before the crystallization only was used to determine the recommended values of the heat capacity of molten poly(oxy-1,4-phenylene). The data on sample 29 from 370-380 K and on both the samples from 590 to 620 K were curve fitted into the equation

$$C_p = 0.1425T + 99.01 \text{ J mol}^{-1}\text{K}^{-1}. \tag{25}$$

The RMS deviation was 1.8%. Equation (25) was used to calculate the heat capacity of molten poly(oxy-1,4-phenylene) from 358 to 620 K. These values are listed in table 28.

Table 27. Recommended heat capacity data for poly(oxy-1,4-phenylene) below the glass transition[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
300.0	109.1
310.0	112.4
320.0	115.8
330.0	119.2
340.0	122.5
350.0	125.9
358.0(T_g)	128.6

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation

2.3.10. Poly(oxy-2,6-dimethyl-1,4-phenylene)

Only one investigation [30] has been reported in the literature which deals with the heat capacity of poly(oxy-2,6-dimethyl-1,4-phenylene). Details of this investigation are given in table 29. Heat capacities of an amorphous sample and a semicrystalline sample ($w^c = 0.25$–0.4) have been measured over the temperature range of 80 to 570 K. The data on these samples are given in table A11. Table A11 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Below the glass transition temperature, the heat capacity of amorphous and semicrystalline samples are in good agreement. Thus the heat capacity of poly(oxy-2,6-dimethyl-1,4-phenylene) below the glass transition temperature is largely independent of crystallinity. The recommended data from 80 to 420 K were derived by averaging the data on samples 31 and 32 at each temperature. The standard deviation was better than 0.1%. The recommended data above 420 K were derived by curve fitting the data on both samples from 400 to 470 K into the equation

$$C_p = 0.3428T + 53.86\ J\ mol^{-1}K^{-1}. \qquad (26)$$

The RMS deviation was 0.7%. Equation (26) was used to calculate the heat capacity from 430 to 482 K. These values are listed in table 30.

The recommended data on heat capacity of molten poly(oxy-2,6-dimethyl-1,4-phenylene) were determined by curve fitting the data on samples 31 and 32 from 490 to 570 K into the equation

$$C_p = 0.2279T + 141.09\ J\ mol^{-1}K^{-1}. \qquad (27)$$

The RMS deviation was 0.4%. Equation (27) was used to calculate the heat capacity of poly(oxy-2,6-dimethyl-1,4-phenylene) from 482 to 570 K. These values are listed in table 31.

2.3.11 Poly(oxy-2,6-diphenyl-1,4-phenylene)

Only one investigation [28] has been reported in the literature which deals with the heat capacity of poly(oxy-2,6-diphenyl-1,4-phenylene). Details of this investigation are given in table 32. Heat capacities of an amorphous sample and a semicrystalline sample ($w^c = 0.52$) have been measured from 180 to 820 K. The amorphous sample crystallizes above the glass transition at 530 K. The data on these samples are given in table A12. Table A12 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Below the glass transition temperature, the heat capacity of amorphous and semicrystalline samples are in good agreement. Thus the heat capacity of poly(oxy-2,6-diphenyl-1,4-phenylene) below the glass transition is largely independent of crystallinity in the range from 180 to 493 K. The averaged values of samples 33 and 34 from 180 to 470 K were taken as the recommended data. These values are listed in table 33. The recommended values above 470 K were derived by curve fitting the data on sample 33 from 420 to 470 K into the equation

$$C_p = 0.612T + 93.39\ J\ mol^{-1}K^{-1}. \qquad (28)$$

The RMS deviation was 0.1%. Equation (28) was used to calculate the heat capacity of poly(oxy-2,6-diphenyl-1,4-phenylene) from 480 to 493 K. These recommended values are listed in table 33.

Amorphous poly(oxy-2,6-diphenyl-1,4-phenylene) crystallizes above the glass transition. Thus the heat capacity data on the amorphous sample above the glass transition temperature and before the crystallization only was used to determine the recommended values of heat capacity of molten poly(oxy-2,6-diphenyl-1,4-phenylene). The data on sample 33 from 500 to 530 K and on sample 34 from 780 to 820 K was curve fitted into the equation

Table 28. Recommended heat capacity data for molten poly(oxy-1,4-phenylene)[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
358.0(T_g)	150.0
360.0	150.3
370.0	151.7
380.0	153.1
390.0	154.6
400.0	156.0
410.0	157.4
420.0	158.8
430.0	160.3
440.0	161.7
450.0	163.1
460.0	164.5
470.0	166.0
480.0	167.4
490.0	168.8
500.0	170.2
510.0	171.7
520.0	173.1
530.0	174.5
535.0(T_m)	175.2
540.0	175.9
550.0	177.4
560.0	178.8
570.0	180.2
580.0	181.6
590.0	183.1
600.0	184.5
610.0	185.9
620.0	187.3

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[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 29. Heat capacity measurements of poly(oxy-2,6-dimethyl-1,4-phenylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Karasz, Bair and O'Reilly (1968) [30]	31. Commercial sample PPO (General Electric) Amorphous sample obtained by cooling from melt at 12 deg h. $\bar{M}_w$=40,000	330-570	Adiabatic (0.5%)	Table[a]
	32. Commercial sample PPO (General Electric) $\bar{M}_w$=40,000 ΔH_f=1.38 kJ mol^{-1} w^c=0.4 (ΔH_f) w^c=0.25 (X-ray)	80-550	Adiabatic (0.5%)	Table[a]

[a] Data were interpolated using the spline function technique to give heat capacities at every ten degree interval.

Table 30. Recommended heat capacity data for poly(oxy-2,6-dimethyl-1,4-phenylene) below the glass transition[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
80.0	53.08
90.0	58.27
100.0	63.46
110.0	68.54
120.0	73.33
130.0	77.66
140.0	82.22
150.0	86.49
160.0	90.64
170.0	94.88
180.0	98.87
190.0	103.3
200.0	107.6
210.0	111.7
220.0	116.0
230.0	119.9
240.0	124.1
250.0	128.3
260.0	132.6
270.0	136.5

Table 30. Recommended heat capacity data for poly(oxy-2,6-dimethyl-1,4-phenylene) below the glass transition[a]--Continued

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
273.15	137.8
280.0	140.7
290.0	145.7
298.15	148.3
300.0	149.7
310.0	153.6
320.0	157.9
330.0	162.1
340.0	166.2
350.0	170.2
360.0	174.5
370.0	178.6
380.0	182.7
390.0	186.8
400.0	190.5
410.0	194.5
420.0	198.2
430.0	201.3
440.0	204.7
450.0	208.1
460.0	211.6
470.0	215.0
480.0	218.4
482(T_g)	219.1

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 31. Recommended heat capacity data for molten poly(oxy-2,6-dimethyl-1,4-phenylene)[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
482.0(T_g)	251.0
490.0	252.8
500.0	255.1
510.0	257.3
520.0	259.6
530.0	261.9
535.0(T_m)	263.0
540.0	264.2
550.0	266.5
560.0	268.7
570.0	271.0

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 32. Heat capacity measurements of poly(oxy-2,6-diphenyl-1,4-phenylene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Wrasidlo (1971) [28]	33. Commercial sample (General Electric) Amorphous sample w^c=0(X-ray); cryst. at 530 K $\bar{M}_v$=143,000	180-780	DSC (3%)[a]	Graph
	34. Commercial sample (General Electric) Cold cryst. at 725 K $\bar{M}_v$=143,000 w^c=0.52 (X-ray)	180-820	DSC (3%)[a]	Graph

[a] Data reported in the form of small graphs. Error in data retrieval increased the uncertainty to 5%.

$$C_p = 0.6887T + 132.18\ \mathrm{J\ mol^{-1}K^{-1}}. \qquad (29)$$

The RMS deviation was 0.5%. Equation (29) was used to calculate the heat capacity of molten poly(oxy-2,6-diphenyl-1,4-phenylene) from 493 to 820 K. These values are listed in table 34.

2.3.12 Poly[oxy-2,2-bis(chloromethyl)trimethylene]

Two investigations [31,32] have been reported in the literature which deal with the heat capacity of poly[oxy-2,2-bis(chloromethyl)trimethylene]. Details of these investigations are given in table 35. Both measurements have been made on highly crystalline commercial samples of the trade name Penton.

To determine the recommended values of poly[oxy-2,2-bis(chloromethyl)trimethylene] the data of Dainton, Evans, Hoare, and Melia [31] from 0 to 310 were made to join the data of Hellwege, Knappe, and Wetzel [32] from 320 to 390 K. The data from reference [31] from 0 to 260 K were taken as the recommended data. To determine the recommended values above 260 K to the glass transition temperature (278 K), the data from reference [31] from 200 to 260 K were curve fitted into the equation

Table 33. Recommended heat capacity data for poly(oxy-2,6-diphenyl-1,4-phenylene) below the glass transition[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
180.0	180.6
190.0	189.2
200.0	198.2
210.0	207.3
220.0	215.9
230.0	223.1
240.0	229.4
250.0	235.9
260.0	243.3
270.0	251.2
273.15	253.8
280.0	259.3
290.0	267.0
298.15	272.8
300.0	274.1
310.0	280.5
320.0	287.0
330.0	294.5
340.0	302.5
350.0	309.5
360.0	315.0
370.0	320.2
380.0	326.3
390.0	333.0
400.0	339.4
410.0	344.8
420.0	350.1
430.0	356.3
440.0	363.0
450.0	369.5
460.0	375.2
470.0	380.3
480.0	387.2
490.0	393.3
493.0(T_g)	395.1

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 34. Recommended heat capacity data for molten poly(oxy-2,6-diphenyl-1,4-phenylene)[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
493.0(T_g)	471.7
500.0	476.5
510.0	483.4
520.0	490.3
530.0	497.2
540.0	504.1
550.0	510.9
560.0	517.8
570.0	524.7
580.0	531.6
590.0	538.5
600.0	545.4
610.0	552.3
620.0	559.2
630.0	566.0
640.0	572.9
650.0	579.8
660.0	586.7
670.0	593.6
680.0	600.5
690.0	607.4
700.0	614.2
710.0	621.1
720.0	628.0
730.0	634.9
740.0	641.8
750.0	648.7
753.0(T_m)	650.7
760.0	655.6
770.0	662.5
780.0	669.3
790.0	676.2
800.0	683.1
810.0	690.0
820.0	696.9

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[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation

Table 35. Heat capacity measurements of poly[oxy-2,2-bis(chloromethyl)trimethylene]

Investigator	Sample no., characterization	Temperature range (K)	Experimentsl technique (claimed uncertainty)	Source of data
Dainton, Evans, Hoare and Melia (1962)[31]	35. Commercial sample: Penton (Hercules)	22-310	Adiabatic (1%)	Table
Hellwege, Knappe and Wetzel (1962) [32]	36. Commercial sample Penton (Hercules)	320-390	Adiabatic (1%)	Graph

Table 36. Recommended heat capacity data for poly[oxy-2,2-bis(chloromethyl)trimethylene])^a

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
0	0.0
10	3.193
20	15.75
30	26.63
40	35.24
50	42.72
60	49.51
70	55.64
80	61.39
90	66.80
100	71.98
110	76.91
120	81.56
130	85.91
140	90.07
150	93.99
160	97.93
170	101.7
180	105.7
190	109.6
200	113.8
210	117.9
220	121.9
230	126.1
240	129.6
250	133.4
260	137.4
270	141.3
273.15	142.5
278	144.4
Glass transition	
278	162.2
280	163.8
290	171.5
298.15	177.1

Table 36. Recommended heat capacity data for poly[oxy 2,2-bis(chloromethyl)trimethylene)][a]--Continued

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
300	178.3
310	184.3
320	189.7
330	194.5
340	198.8
350	202.7
360	206.1
370	209.2
380	212.0
390	214.5

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 37. Heat capacity contribution of -O- group in $J\ mol^{-1}K^{-1}$ in the crystalline state calculated from data on various polyoxides and polyethylene

T(K)	POM[a]	POM_2[b]	POM_3[c]	POM_4[d]	POM_8[e]	PO_2M_3[f]	PO_2M_5[g]
10	0.32		0.57	1.08			
20	1.73		2.49	3.67	3.30		
30	3.57		3.80	5.07	5.14		
40	4.79		4.09	5.57	5.61		
50	5.58		4.07	6.54	6.56		
60	6.11		4.14	6.76	7.31		
70	6.47		5.33	7.29	7.94		
80	6.75		6.22	8.25	9.63		
90	6.99	7.59	6.93	9.05	10.53		
100	7.23	8.02	7.51	9.46	11.24	6.42	6.60
110	7.48	8.38	7.98	9.92	11.34	6.82	7.14
120	7.76	8.60	8.35	11.02	11.69	7.15	7.74
130	8.11	8.90	8.71	11.59	11.90	7.50	8.39
140	8.50	9.07	9.08	12.12	12.50	7.89	9.06
150	8.95	9.31	9.50	12.98	13.14	8.26	9.71
160	9.44	9.63	10.02	14.16	13.20	8.76	10.35
170	9.97	9.82	10.65	15.20	14.70	9.31	11.22
180	10.52	10.05	11.38	16.40	15.56	9.96	12.19
190	11.06	10.30			17.00	10.69	
200	11.58	10.74			18.94	11.84	

Table 37. Heat capacity contribution of -O- group in J $mol^{-1}K^{-1}$ in the crystalline state calculated from data on various polyoxides and polyethylene -- Continued

T(K)	POM^a	$POM_2{}^b$	$POM_3{}^c$	$POM_4{}^d$	$POM_8{}^e$	$PO_2M_3{}^f$	$PO_2M_5{}^g$
210	12.08	10.97			20.60		
220	12.54	11.32			22.42		
230	12.96				25.80		
240	13.36						
250	13.74						
260	14.16						
270	14.64						
280	15.21						
290	15.90						
300	16.71						
310	17.64						
320	18.66						
330	19.71						
340	20.70						
350	21.52						
360	22.06						
370	22.25						
380	22.08						
390	21.64						

[a] Poly(oxymethylene) - Polyethylene

[b] Poly(oxyethylene) - 2 Polyethylene

[c] Poly(oxytrimethylene) - 3 Polyethylene

[d] Poly(oxytetramethylene) - 4 Polyethylene

[e] Poly(oxyoctamethylene) - 8 Polyethylene

[f] [Poly(oxymethyleneoxyethylene) - 3 Polyethylene]/2

[g] [Poly(oxymethyleneoxytetramethylene) - 5 Polyethylene]/2

$$C_p = 0.3871T + 36.74 \text{ J mol}^{-1}\text{K}^{-1}. \quad (30)$$

The RMS deviation was 0.1%. Equation (30) was used to calculate the heat capacity from 260 to 278 K.

The heat capacity data above the glass transition were obtained by curve fitting the data from reference [31] from 280 to 310 K and from reference [32] from 320 to 390 K into the equation

$$C_p = -1.0060T^{-2} - 0.10473T + 321.48 \text{ J mol}^{-1}\text{K}^{-1}. \quad (31)$$

The RMS deviation was 1.5%. Equation (31) was used to calculate the heat capacity above the glass transition temperature (278 K) to 390 K. These recommended values are listed in table 36.

3. Heat Capacity Contribution of the –O– Group

The heat capacity data on polyoxides have been further analyzed to determine the heat capacity contribution of the –O– group which can be used in a heat capacity addition scheme [21,22]. By comparing the heat capacity data of simple polyoxides of type $(CH_2)_x$–O–$(CH_2)_y$–O– with polyethylene (discussed in ref. [2]), the heat capacity of the –O– group in the crystalline and the molten state has been evaluated. These data are listed in tables 37 and 38.

In the crystalline state of polyoxides where the –O– group constitutes 25% or more of the backbone atoms [poly(oxymethylene), poly(oxyethylene), poly(oxytrimethylene), poly(oxymethyleneoxyethylene) and poly(oxymethyleneoxyethylene)], the heat capacity contribution of the –O– groups are in good agreement above 20 K. However, the heat capacity contribution of the –O– group in polyoxides with larger sequences of CH_2– groups [poly(oxytetramethylene) and poly(oxyoctamethylene)], is larger and approaches the heat capacity of the CH_2– group. This may be a sign that the frequency distribution of the skeletal vibrations in polyoxides approaches that of polyethylene with increasing length of the CH_2– sequence [13].

Table 38. Heat capacity contribution of -O- group in J $mol^{-1}K^{-1}$ in the molten state calculated from data on various polyoxides and polyethylene

T(K)	POM_2[a]	POM_3[b]	POM_4[c]	PO_2M_3[d]	PO_2M_5[e]
250	32.38	28.10	19.61	22.17	21.02
260	31.97	27.81	19.60	22.08	20.83
270	31.55	27.52	19.59	21.98	20.64
280	31.14	27.23	19.59	21.89	20.45
290	30.73	26.94	19.58	21.79	20.26
300	30.32	26.66	19.57	21.69	20.08
310	29.91	26.37	19.56	21.60	19.89
320	29.50	26.08	19.56	21.50	19.70
330	29.09	25.79	19.55	21.41	19.51
340	28.68		19.54	21.31	19.32
350	28.26			21.22	19.13
360	27.85			21.12	18.95
370	27.44			21.02	
380				20.93	
390				20.83	

[a] Poly(oxyethylene) - 2 Polyethylene

[b] Poly(oxytrimethylene) - 3 Polyethylene

[c] Poly(oxytetramethylene) - 4 Polyethylene

[d] [Poly(oxymethyleneoxyethylene) - 3 Polyethylene]/2

[e] [Poly(oxymethyleneoxytetramethylene - 5 Polyethylene]/2

In case of molten poly(oxides), the heat capacity contribution of the -O- group decreases with temperature. The contribution from poly(oxytetramethylene), poly(oxymethyleneoxyethylene) and poly(oxymethyleneoxytetramethylene) are again constant within the error limits [the heat capacity of the -O- group in poly(oxyoctamethylene) from the limited data: 19.42 (at 350 K) and 17.78 (at 360 K) are also in good agreement]. The heat capacity contribution of the -O- group from poly(oxyethylene) and poly(oxytrimethylene) are somewhat higher.

Heat capacity in the molten state has an added contribution besides vibrational heat capacity—the hole contribution. Vibrational contributions are usually additive [21], but the hole contribution to the heat capacity may not be additive. A measure of the hole contribution to the heat capacity is the change (ΔC_p) at the glass transition temperature (discussed in sect. 4). The changes ΔC_p for poly(oxytetramethylene), poly(oxymethyleneoxyethylene) and poly(oxymethyleneoxytetramethylene) per chain atom are in good agreement ($\Delta C_p = 10.2 \pm 0.9$ J $mol^{-1}K^{-1}$ bead), leading as a result also to similar heat capacity contributions due to holes and thus making the heat capacity additive. Poly(oxyethylene) and poly(oxytrimethylene) have a higher ΔC_p, 14.28 and 12.68 J $mol^{-1}K^{-1}bead^{-1}$, respectively, and we observe a somewhat higher heat capacity contribution of the -O- group.

The analysis of the heat capacity of molten polyoxides in terms of size, number and energy of holes, packing fraction and cohesive energy density has been reported elsewhere [22].

The overall decrease in the heat capacity contribution of the -O- group with temperature in molten states is related to the decreasing contribution of the hole equilibrium to the heat capacity [13]. The same decrease was observed for the heat capacity of liquid selenium [1], the only monatomic flexible, linear macromolecule analyzed.

4. Conclusions

The heat capacity of poly(oxymethylene), poly(oxyethylene), poly(oxytrimethylene), poly(oxytetramethylene), poly(oxypropylene), poly(oxymethyleneoxyethylene), poly(oxymethyleneoxytetramethylene), poly(oxy-1,4-phenylene), poly(oxy-2,6-dimethyl-1,4-phenylene), poly(oxy-2,6-diphenyl-1,4-phenylene) and poly[oxy-2,2-bis(chloromethyl)trimethylene] is reviewed on hand of 35 measurements reported in the literature. A set of recommended data is derived for each polyoxide (plotted in figs. 2 and 3). Entropy, enthalpy, and Gibbs energy are calculated where possible. We have arrived in addition at the following conclusions:

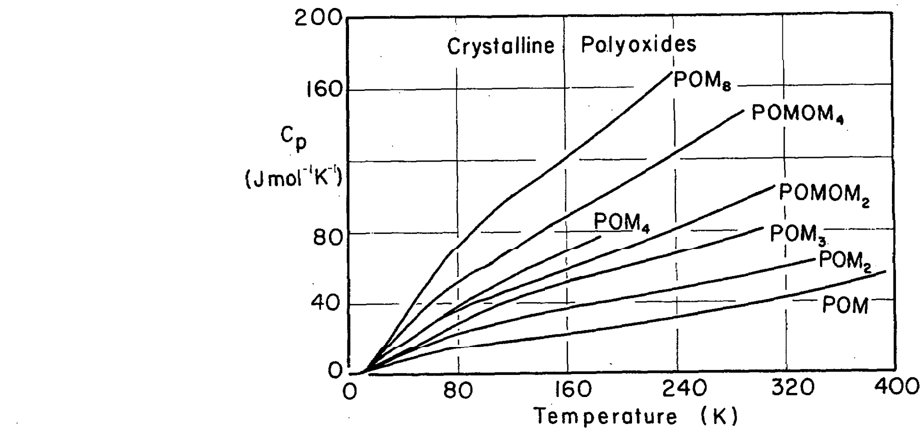

Figure 2. Recommended data on the heat capacity of crystalline polyoxides of type (CH$_2$–)$_x$O–(CH$_2$–)$_y$O–

POM = Poly(oxymethylene)
POM$_2$ = Poly(oxyethylene)
POM$_3$ = Poly(oxytrimethylene)
POM$_4$ = Poly(oxytetramethylene)
POM$_8$ = Poly(oxyoctamethylene)
POMOM$_2$ = Poly(oxymethyleneoxyethylene)
POMOM$_4$ = Poly(oxymethyleneoxytetramethylene)

1. The heat capacities of crystalline poly(oxymethylene), poly(oxyethylene), poly(oxytrimethylene), poly(oxymethyleneoxyethylene) and poly(oxymethyleneoxytetramethylene) were found to be additive above 20 K. The heat capacities of polyoxides with longer sequences of CH$_2$– units [poly(oxytetramethylene) and poly(oxyoctamethylene)] tend towards the values for polyethylene.

2. In the molten state, the heat capacities are additive only if the heat capacity changes at the glass transition temperature are similar.

3. For poly(oxytrimethylene), the extrapolated heat capacity of the completely amorphous polymer below the glass transition temperature is higher than the extrapolated heat capacity of the completely crystalline polymer. The differences are, however, small (less than 4%) from 90 to 180 K. At 0 K, the residual amorphous entropy is 3.91 J mol^{-1}K^{-1}. For other polyoxides complete data sets are not available.

4. The change in heat capacity at the glass transition temperature is listed in table 39. Poly(oxytrimethylene), poly(oxytetramethylene), poly(oxymethyleneoxyethylene), poly(oxymeth-

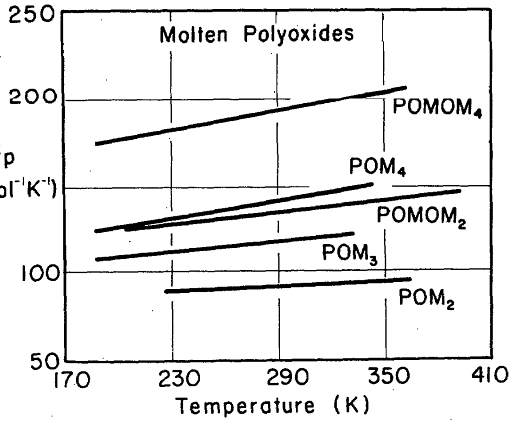

Figure 3. Recommended data on the heat capacity of molten polyoxides of type (CH$_2$–)$_x$O–(CH$_2$–)$_y$O–

POM$_2$ = Poly(oxyethylene)
POM$_3$ = Poly(oxytrimethylene)
POM$_4$ = Poly(oxytetramethylene)
POMOM$_2$ = Poly(oxymethyleneoxyethylene)
POMOM$_4$ = Poly(oxymethyleneoxytetramethylene)

Table 39. Heat capacity change at glass transition temperature[a]

Polyoxide	T_g(K)	C_p($Jmol^{-1}K^{-1}$)	No. of beads[b]	ΔC_p/bead ($J\ mol^{-1}K^{-1}\ bead^{-1}$)
Poly(oxyethylene)	232	42.84	3	14.28
Poly(oxytrimethylene)	195	50.73	4	12.68
Poly(oxytetramethylene)	189	46.49	5	9.30
Poly(oxymethyleneoxyethylene)	209	53.44	5	10.69
Poly(oxymethyleneoxytetramethylene)	189	73.90	7	10.55
Poly(oxy-1,4-phenylene)	358	21.40	2	10.70
Poly(oxy-2,6-dimethyl-1, 4-phenylene)	482	31.90	2	15.95
Poly(oxy-2,6-diphenyl-1, 4-phenylene)	493	76.60	4	19.15
Poly(oxypropylene)	198	32.15	3	10.71

[a] According to Wunderlich's rule of constant heat capacity change at glass transition temperature ΔC_p = 11.3 ± 2.1 J mol^{-1} k^{-1} $bead^{-1}$

[b] Bead is defined as a smallest section of the molecule that can move independently as a unit in internal rotation.

yleneoxytetramethylene), poly(oxypropylene), and poly(oxy-1,4-phenylene) are in good agreement with Wunderlich's rule of constant ΔC_p (11.3 ± 2.1 J $mol^{-1}K^{-1}$ $bead^{-1}$) [46]. ΔC_p for poly(oxyethylene), poly(oxy-2,6-dimethyl-1,4-phenylene), and poly(oxy-2,6-diphenyl-1,4-phenylene) are somewhat higher. Wrasidlo [47] has found similar deviations for ladder-type polymers which contain large numbers of benzene rings.

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