

Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules VI. Acrylic Polymers

Cite as: Journal of Physical and Chemical Reference Data **11**, 1065 (1982); <https://doi.org/10.1063/1.555671>
Published Online: 15 October 2009

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Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules

VI. Acrylic Polymers

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Heat capacity of poly(methyl methacrylate), polyacrylonitrile, poly(methyl acrylate), poly(ethyl acrylate), poly(n-butyl acrylate), poly(iso-butyl acrylate), poly(octadecyl acrylate), poly(methacrylic acid), poly(ethyl methacrylate), poly(n-butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(dodecyl methacrylate), poly(octadecyl methacrylate) and polymethacrylamide is reviewed on the basis of measurements on 35 samples reported in the literature. A set of recommended data are derived for each acrylic polymer in the amorphous state. Enthalpy and entropy functions are calculated for poly(methyl methacrylate) and polyacrylonitrile. This is the sixth paper in a series of publications which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: enthalpy; entropy; glass transition; heat capacity; linear macromolecule; polyacrylate; polyacrylonitrile; polymethacrylamide; polymethacrylate; poly(methacrylic acid).

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1. Introduction

This is the sixth paper in a series of discussions on the heat capacity of linear macromolecules. In the earlier papers [1-5]², the heat capacity of selenium, polyethylene, polypropylene, polystyrene and various types of polyoxides have been analyzed. This paper deals with acrylic polymers. In subsequent papers heat capacity of all other polymers with carbon backbone, polyamides, polyesters and polymers containing aromatic groups and/or inorganic chain atoms will be evaluated.

2. Heat Capacity of Acrylic Polymers

2.1. Introduction

Acrylic polymers are usually atactic and thus amorphous over the whole temperature region. Heat capacities of

isotactic polymers have not been reported. The acrylic polymers which have been analyzed in this study are listed in table 1 [6,7,8]. For acrylic polymers with long side chain (more than 10-12 carbon atoms), side chain crystallinity is observed [8,9]. The glass transition temperature of this kind of polymer with side groups usually decreases as the length of the side group increases. Reimschuessel [8] has derived several empirical equations which correlate the glass transition temperature with the number of carbon atoms in the side chain. It was found that the glass transition temperature decreases monotonically as the length of the alkyl side-chain increases toward a critical length. The critical length is different for different kinds of polymer backbones (e.g., 9 for poly(alkyl acrylate) and 12 for poly(alkyl methacrylate). Reimschuessel [8] suggested that the decrease in glass transition temperature is due to the interaction of the backbone and the side chain. An increase in the length of the side chain will result in a larger free volume, a reduced packing density, and thus a reduced steric hindrance to mobility. As the side chain length increases beyond the critical length, a renewed increase in the glass transition temperature is seen, now mainly due to decreasing side chain mobility. Finally the glass transition temperature has to approach the glass transition temperature of polyethylene as the side chain becomes much longer.

¹See AIP document no. PAPS JPCRD-11-1065-26 for 26 pages of data tables. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 355 East 45th Street, New York, N.Y. 10017. The price is \$1.50 for a microfiche or \$5.00 for photocopies. Airmail is additional. This material also appears in *Current Physics Microform*, the monthly microfilm edition of the complete set of journals published by AIP, on the frames following this journal article.

²Numbers in brackets refer to the literature references cited in section 4.

Table 1. Acrylic polymers investigated in this study

Name, formula wt., and structure of the repeat unit	T_g or T_m^a (K)	Abbreviation used throughout the paper
Poly(methyl acrylate) (86.09) $\text{CH}_2\text{-CH}(\text{COOCH}_3)\text{-}$	279	PMA
Poly(ethyl acrylate) (100.12) $\text{CH}_2\text{-CH}(\text{COOC}_2\text{H}_5)\text{-}$	249	PEA
Poly(n-butyl acrylate) (128.17) $\text{CH}_2\text{-CH}(\text{COOC}_4\text{H}_9)\text{-}$	216	PNBA
Poly(iso-butyl acrylate) (128.17) $\text{CH}_2\text{-CH}(\text{COOC}_4\text{H}_9)\text{-}$	249	PIBA
Poly(octadecyl acrylate) (324.55) $\text{CH}_2\text{-CH}(\text{COOC}_{18}\text{H}_{37})\text{-}$	332 ^a	PODA
Poly(methacrylic acid) (86.10) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOH})\text{-}$	501	PMAA
Poly(methyl methacrylate) (100.12) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOCH}_3)\text{-}$	378 ^b	PMMA
Poly(ethyl methacrylate) (114.15) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOC}_2\text{H}_5)\text{-}$	338 ^c	PEMA
Poly(n-butyl methacrylate) (142.20) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOC}_4\text{H}_9)\text{-}$	293 ^d	PNBMA
Poly(iso-butyl methacrylate) (142.20) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOC}_4\text{H}_9)\text{-}$	326 ^e	PIBMA
Poly(hexyl methacrylate) (170.23) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOC}_6\text{H}_{13})\text{-}$	268	PHMA
Poly(dodecyl methacrylate) (254.52) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOC}_{12}\text{H}_{25})\text{-}$	240 ^f	PDDMA
Poly(octadecyl methacrylate) (338.58) $\text{CH}_2\text{-C}(\text{CH}_3)(\text{COOC}_{18}\text{H}_{37})\text{-}$	313 ^a	PODMA
Polyacrylonitrile (53.06) $\text{CH}_2\text{-CH}(\text{CN})\text{-}$	378	PAN
Poly(methacrylamide) (85.11) $\text{-CH}_2\text{-C}(\text{CH}_3)(\text{CONH}_2)\text{-}$		PMAM

^a T_m of the side chain^b T_g (isotactic) = 318-328K, T_g (syndiotactic) = 388 K.^c T_g (isotactic) = 285 K^d T_g (isotactic) = 249 K^e T_g (isotactic) = 281 K^freference [8]

For the side chain melting of acrylic polymers with sufficiently long side groups, a general pattern of the melting temperature versus number of carbon atoms in the side chain is observed. (See for example, ref. 9.) Macromolecules with a side chain which contains above ten carbon atoms have melting points close to those of alkanes of similar length. The backbone of the atactic acrylic polymer does not participate in the crystallization of the side chain. As the length of the side chain increases, the melting point drifts to a higher value which is closer to those of alkanes of double the chain length (this happens when the carbon atom of side chain is about 28 for acrylic polymer).

2.2. Literature Data on Heat Capacity of Acrylic Polymers

Thirty-nine investigations have been reported in the literature on heat capacity measurements of various types of acrylic polymers. Heat capacities of over 53 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 19 of the 39 investigations met our standards of acceptable data (discussed in ref. [1]).

These contain heat capacity data on 35 samples of 14 types of acrylic polymers. Twenty 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 Acrylic Polymers

2.3.1. Poly(methyl methacrylate)

Fifteen investigations [32–34, 37–48] have been reported in the literature which deal with the heat capacity of poly(methyl methacrylate). Details of these investigations are given in table 3. Heat capacity of 11 amorphous samples have been measured over the temperature range of 0.15 to 550 K. The data of these samples are given in tables 1A, 2A, and 3A. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. The low temperature data (below 5 K) are given in table 1A. Tables 2A and 3A contain data on poly(methyl methacrylate) below and above the glass transition temperature.

Heat capacity measurements on four amorphous samples have been reported below 5 K. All the data (table 1A) on these samples (15, 17, 21 and 24) were compared on a logarithmic plot. The data are in fair agreement with one another with the exception of Reese's data on sample 17. Reese's data are consistently higher than the data on all other samples by 25–48%. Measurements on sample 17 were made using the transient technique in which the heat capacity is measured indirectly from thermal conductivity. The data on all other samples were obtained using the heat pulse method. Since the heat pulse method is considered more reliable than the transient technique (see ref. [1]), the data on sample 17 were not used. Similar deviations of the order of 25–40% were found for Reese's data on polystyrene [5].

The recommended data on the heat capacity of amor-

phous poly(methyl methacrylate) below 4 K were determined by curve fitting the data on samples 15, 21, and 24 from 0.2 to 4.0 K into the equation

$$C_p = \exp[-0.0728327(\ln T)^3 + 0.364455(\ln T)^2 + 2.74468(\ln T) - 5.81873] \text{ J mol}^{-1} \text{ K}^{-1}. \quad (1)$$

The RMS deviation was 11.4%. Equation (1) was used to evaluate the heat capacity of amorphous poly(methyl methacrylate) from 0.1 to 5 K. These values are listed in table 4.

In the preliminary analysis to determine the recommended data for poly(methyl methacrylate) from 20 K to the glass transition, all heat capacity data (table 2A) were plotted on a composite plot. It was found that the data were in quite good agreement over the entire temperature range with the exception of Sochava and Trapeznikov's data (sample 14) and Rabinovich and Lebedev's data (sample 20) from 190 to 300 K and Pavlinov et al.'s data on sample 18 from 290 to 360 K. The deviations are of the order of 2–12%. Similar deviations were found for Sochava and Trapeznikova's data on poly(methyl acrylate) and poly(methacrylic acid). All other 93 data points agree within $\pm 1\%$. To determine the recommended data on the heat capacity of poly(methyl methacrylate) below the glass transition temperature, the latter data from 60 to 370 were averaged at each temperature. The standard deviation was less than 1%. From 20 to 50 K, the only data available on sample 14 are recommended.

The heat capacity of amorphous poly(methyl methacrylate) from 60 to 370 K obtained by averaging the data on various samples below the glass transition temperature were further smoothed as follows: Average heat capacity values from 60 to 200 K were curve fitted into the equation

$$C_p = \exp[0.248904(\ln T)^3 - 3.68228(\ln T)^2 + 18.8875(\ln T) - 29.1454] \text{ J mol}^{-1} \text{ K}^{-1}. \quad (2)$$

The RMS deviation was 0.8%. The data from 150 to 370 K were curve fitted into the equation

$$C_p = 1.90245 \times 10^4 T^{-2} + 0.404624T + 16.1182 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (3)$$

The RMS deviation was 0.3%. The smoothed values obtained from 0.1 to 5 K, obtained from eq (1), from 60 to 180 K, obtained from eq (2) and from 190 to the glass transition temperature (378 K), obtained from eq (3), and data on sample 14 from 20 to 60 K are given in table 4.

To determine the recommended heat capacity data on molten poly(methyl methacrylate), the data on all molten samples were plotted. Agreement between the data on samples 16, 25, and 26 is quite good. However, the data of Hoffmann and Knappe on sample 22 and the data of Pavlinov et al. on sample 18 show large deviations (3–5%). These data were omitted. Hoffmann and Knappe's data on other molten acrylic polymers also shows deviations (sec. 2.3.3) and the data of Pavlinov et al. on glassy poly(methyl methacrylate) also shows large deviations.

The recommended data on the heat capacity of molten poly(methyl methacrylate) were determined by curve fitting the data on samples 16, 25, and 26 from 320 to 550 K into the

Table 2. Investigations not included in this study^a

References	Reason(s) for exclusion
Gucker and Ford (1938) [10]	Single room temperature heat capacity value reported.
Hellwege et al. (1959) [11]	Sample characterization not reported Data superseded by later publication [12].
Tautz et al. (1963, 1964) [13, 14]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Karasev (1967) [15]	Data could not be read accurately from too small graphs.
Goetze et al. (1967) [16]	Heat capacity data reported in polyacrylonitrile fibers in humid conditions.
Griskey and Hubbel (1968) [17]	Data reported for poly(methyl methacrylate), poly(diethylaminoethyl methacrylate), poly(cyclohexyl methacrylate), poly(allyl methacrylate), and poly(ethyl acrylate) from 400 to 570 K. The measurements seem to be reasonable at low temperatures, however, show an unexplained sharp increase (more than 100%) at higher temperatures.
Luikov et al. (1971) [18]	Indirect measurement of heat capacity from thermal diffusivity (claimed uncertainty 5%).
Urzendowski et al. (1971) [19]	Heat capacity reported for poly(methyl methacrylate), poly(ethyl methacrylate) and poly(n-butyl methacrylate). Their data show large deviation (3-7%) from the data recommended here.

Table 2. Investigations not included in this study^a--Continued

References	Reason(s) for exclusion
Anderson and Sundquist (1975) [20]	The pressure dependence of heat capacity of poly(methyl methacrylate) was determined from simultaneous measurements of thermal conductivity and diffusivity at 300 K in the pressure range 0-25 kbar. The heat capacity decreases with increasing pressure, and its value at 25 kbar is 0.93 times that at atmospheric pressure.
Bashirov et al. (1975, 1976) [21, 22]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Pasquini et al. (1975, 1976) [23, 24]	Data reported for poly(phenyl acrylate). These publications are not available in our data bank.
Lai (1976) [25]	Besides heat capacity measurements on poly(hexyl methacrylates) discussed in section 2.3.3., data also reported for molten poly(glycidyl methacrylate) over a limited temperature range (350 to 400 K).
Belostotskii et al. (1976, 1977) [26, 27]	Heat capacity reported at 303 to 363 K as a function of pressure (0-5 bar).
Boucha et al. (1976) [28]	Heat capacity data reported as a function of mechanical history.
Shubin (1977) [29]	Heat capacity reported from 323 to 523 K as a function of pressure (0-2 kbar).
Dushchenko et al. (1977, 1978) [30, 31]	Heat capacity in the glass transition region reported as a function of thermal history. The effects of isothermal annealing and heating rate have been evaluated.

^aUnless otherwise noted, all the publications refer to data on poly(methyl methacrylate).

Table 3. Heat capacity measurements of poly(methyl methacrylate)

Investigator	Sample No. characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Sochava and Trapaznikova (1958, 1961, 1965) [32, 33, 34]	14. Amorphous	16-250	Adiabatic (unreported)	Table [35,36]
Noer et al. (1959) [37]	15. Amorphous	1.4-4.2	Heat Pulse (5%)	Equation ^a
O'Reilly and Karasz (1966) [38,39]	16. Average data for three amorphous samples (abatic $T_g = 322$; syndiotactic $T_g = 390$ K)	230-410	Adiabatic (0.4%)	Graph
Reese (1966) [40]	17. Amorphous	1.0-4.5	Transient Method (10%)	Equation ^b
Pavlinov et al. (1967) [41]	18. Amorphous $T_g = 378$ K	290-430	Adiabatic (0.5%)	Equation ^c
Rabinovich and Lebedev (1967) [42,43,44]	20. Amorphous $\bar{M}_v = 162,000$	60-300	Adiabatic (0.5%)	Table
Choy et al. (1970) [45]	21. Amorphous $\bar{M}_n = 146,000$ $\bar{M}_w = 1,300,000$ $\rho = 1,185 \text{ Mg m}^{-3}$	0.8-4.0	Heat Pulse (5%)	Table
Hoffmann and Knappe (1971) [46]	22. Amorphous	100-430	Adiabatic (1%)	Graph ^d
Stephens et al. (1972) [47]	24. Amorphous	0.15-4.0	Heat Pulse (5%)	Table
Bares and Wunderlich (1973) [48]	25. Amorphous $\bar{M}_n = 160,000$ $\bar{M}_w = 322,000$	330-550	DSC (1%)	Table
Gaur and Wunderlich [7]	26. Amorphous $\bar{M}_w = 60,600$ $\bar{M}_n = 33,200$	230-500	DSC (1%)	Table ^e

$$^a C_p = 8.4 \cdot 10^{-6} T^3 \text{ cal g}^{-1} \text{ K}^{-4}$$

$$^b C_p = 446 T^3 \text{ ergs cm}^{-3} \text{ K}^{-4}$$

$$^c C_p = 0.264 + 1.39 + 1.39 \cdot 10^{-3} (T-273) \text{ cal g}^{-1} \text{ K}^{-1} \text{ (290-360K)}$$

$$^c C_p = 0.383 + 9.35 \cdot 10^{-3} (T-273) \text{ cal g}^{-1} \text{ K}^{-1} \text{ (400-430K)}$$

^d Straight lines drawn through the heat capacity temperature plot to retrieve the data.

^e Average of two measurements

Table 4. Recommended thermodynamic data for amorphous

T(K)	poly(methyl methacrylate) ^a		
	C_p^a	$H_T^a - H_O^a$	$S_T^a - S_O^a$
	(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)
0.0	0.0	0.0	0.0
0.2	0.0001248	0.0000125	0.0000624
0.3	0.0002101	0.0000292	0.0001286
0.4	0.0003451	0.0000570	0.0002068
0.5	0.0005411	0.0001013	0.0003040
0.6	0.0008120	0.0001690	0.0004258
0.7	0.001173	0.0002682	0.0005772
0.8	0.001641	0.0004089	0.0007636
0.9	0.002234	0.0006027	0.0009903
1.0	0.002971	0.0008629	0.001263
1.2	0.004959	0.001656	0.001973
1.4	0.007776	0.002929	0.002942
1.6	0.01161	0.004868	0.004223
1.8	0.01667	0.007639	0.005843
2.0	0.02316	0.01157	0.007896
3.0	0.08543	0.06586	0.02792
4.0	0.2215	0.2193	0.06985
10.0	1.667	5.914	0.7391
20.0	7.965	54.12	3.5690
30.0	14.67	167.3	8.005
40.0	21.38	347.6	13.12
50.0	27.67	592.	18.56
60.0	34.53	903.	24.21
70.0	41.30	1283.	30.03
80.0	47.29	1726.	35.94
90.0	52.63	2226.	41.82
100.0	57.48	2776.	47.62
110.0	61.96	3373.	53.31
120.0	66.18	4014.	58.88
130.0	70.20	4696.	64.34
140.0	74.10	5417.	69.69
150.0	77.93	6178.	74.93
160.0	81.74	6976.	80.08
170.0	85.55	7812.	85.15
180.0	89.40	8687.	90.15
190.0	93.52	9602.	95.10
200.0	97.52	10556.	99.99
210.0	101.5	11551.	104.8
220.0	105.5	12586.	109.7
230.0	109.5	13661.	114.4
240.0	113.6	14777.	119.2
250.0	117.6	15933.	123.9
260.0	121.6	17129.	128.6
270.0	125.6	18365.	133.3

Table 4. Recommended Thermodynamic data for amorphous
poly(methyl methacrylate)^a--Continued

T(K)	C_p^a (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)
273.15	126.9	18769.	134.8
280.0	129.7	19641.	137.9
290.0	133.7	20958.	142.5
298.15	137.0	22068.	146.3
300.0	137.7	22316.	147.1
310.0	141.7	23713.	151.7
320.0	145.8	25150.	156.3
330.0	149.8	26628.	160.8
340.0	153.9	28147.	165.4
350.0	157.9	29706.	169.9
360.0	161.9	31305.	174.4
370.0	166.0	32944.	178.9
378.0(T _g)	169.2	34285.	182.5
378.0(T _g)	202.7	34285.	182.5
380.0	203.2	34691.	183.5
390.0	205.5	36734.	188.8
400.0	207.9	38801.	194.1
410.0	210.3	40892.	199.2
420.0	212.7	43007.	204.3
430.0	215.0	45146.	209.4
440.0	217.4	47308.	214.3
450.0	219.8	49494.	219.2
460.0	222.2	51704.	224.1
470.0	224.5	53937.	228.9
480.0	226.9	56194.	233.7
490.0	229.3	58475.	238.4
500.0	231.7	60780.	243.0
510.0	234.0	63109.	247.6
520.0	236.4	65461.	252.2
530.0	238.8	67837.	256.7
540.0	241.1	70236.	261.2
550.0	243.5	72659.	265.6

^aThe table 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.

equation

$$C_p = 0.2374 T + 112.95 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (4)$$

The RMS deviation was 0.6%. Equation (4) was used to evaluate the heat capacity of molten poly(methyl methacrylate) from 378 to 550 K. These values are listed in table 4. H_o^a and S_o^a refer to zero point enthalpy and entropy of the amorphous polymer. Details of the integrations have been reported earlier in reference [1].

2.3.2. Polyacrylonitrile

Three investigations [50–52] have been reported in the literature which deal with the heat capacity of polyacrylonitrile. Details of these investigations are given in table 5. The heat capacity of two samples have been measured over the temperature range of 60 to 400 K. The data on these samples are given in table 4A. Table 4A has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Since very limited heat capacity data are available above the glass transition (only from 390–400 K), the recommended heat capacity data are derived only below the glass transition.

The recommended data on the heat capacity of glassy polyacrylonitrile were obtained by curve fitting the data on samples 38 and 39 from 60 to 370 K into the equation

$$C_p = \exp[0.222649(\ln T)^3 - 3.36593(\ln T)^2 + 17.6347(\ln T) - 28.1638] \text{ J mol}^{-1} \text{ K}^{-1}. \quad (5)$$

The RMS deviation was 1.1%. Equation (5) was used to evaluate the heat capacity of glassy polyacrylonitrile from 60 to 370 K. These values are listed in table 6.

Preliminary data on glassy polyacrylonitrile below 60 K were obtained from the curve fitted Tarasov equation reported by Lebedev et al. [50] for sample 38.

$$C_p = 2R \left\{ D_1 \left(\frac{469}{T} \right) - \frac{187.6}{469} \left[D_1 \left(\frac{187.6}{T} \right) - D_3 \left(\frac{187.6}{T} \right) \right] \right\} \quad (6)$$

These data are also listed in table 6.

The recommended heat capacity data were integrated to obtain enthalpy and entropy functions. These are also listed in table 6.

2.3.3. Other Acrylic Polymers

Eight investigations [7, 25, 34, 41–43, 46, 51] have been reported in the literature which deal with the heat capacity of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(n-butyl acrylate) (PNBA), poly(iso-butyl acrylate) (PIBA), poly(octadecyl acrylate) (PODA), poly(methacrylic acid) (PMAA), poly(ethyl methacrylate) (PEMA), poly(n-butyl methacrylate) (PNBMA), poly(iso-butyl methacrylate) (PIBMA), poly(hexyl methacrylate) (PHMA), poly(dodecyl methacrylate) (PDDMA), poly(octadecyl methacrylate) (PODMA) and polymethacrylamide (PMAM). Details of these investigations are given in tables 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, and 19, respectively. Heat capacity has been measured for 22 samples over the temperature range of 60 to 500 K. The data on these samples are given in tables 5A, 6A, 7A, 8A, 9A, 10A, 11A, 12A, 13A, 14A, 15A, 16A, 17A, and 18A. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

The recommended data on all these acrylic polymers in their glassy and molten states were determined by curve fitting the data below and above the glass transition, respectively. These data are listed in tables 20–23.

The results of curve fittings used to derive the recommended data are given in table 24. The equations used for curve fitting are listed separately in table 25. Also listed in table 24 are the RMS deviations and the number of data points used in curve fitting. The data points not used for curve fitting the literature data to derive equations for recommended data for PMA, PEA, PIBA, PMAA, and PEMA are also listed in table 24.

The data of Sochava and Trapeznikova on PMA and PMAA from 50 to 210 K are in good agreement with the recommended data below 120 K, but at higher temperatures show large deviations (up to 10% at 210 K). Since other acceptable data are available for both PMA and PMAA, the data of Sochava and Trapeznikova were rejected over the

Table 5. Heat capacity measurements of polyacrylonitrile

Investigator	Sample no. characterization	Temperature range	Experimental technique (claimed uncertainty)	Source of data
Lebedev et al. (1967) [50]	38. Amorphous $\bar{M}_v = 140,000$	60–300	Adiabatic (0.2%)	Table
Sheiman et al. (1972) [51, 52]	39. Amorphous	80–400	Adiabatic (0.4%)	Graph

Table 6. Recommended thermodynamic data for glassy

polyacrylonitrile ^a			
T(K)	C _p	H _T ^a -H _O ^a	S _T ^a -S _O ^a
	(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)
0.0	0.0	0.0	0.0
10.0	1.172	5.860	0.5860
20.0	1.926	21.35	1.654
30.0	4.941	55.69	2.959
40.0	9.546	128.1	4.975
50.0	13.77	244.7	7.546
60.0	18.09	404.0	10.43
70.0	21.69	602.9	13.49
80.0	24.87	835.7	16.59
90.0	27.69	1099.	19.68
100.0	30.23	1388.	22.73
110.0	32.54	1702.	25.72
120.0	34.68	2038.	28.65
130.0	36.69	2395.	31.50
140.0	38.60	2771.	34.29
150.0	40.44	3167.	37.02
160.0	42.24	3580.	39.69
170.0	44.01	4011.	42.30
180.0	45.76	4460.	44.87
190.0	47.51	4926.	47.39
200.0	49.27	5410	49.87
210.0	51.05	6431.	52.32
220.0	52.86	6431.	54.74
230.0	54.69	6969.	57.13
240.0	56.57	7526.	59.49
250.0	58.48	8101.	61.84
260.0	60.44	8695.	64.17
270.0	62.46	9310.	66.49
273.15	63.09	9508.	67.22
280.0	64.52	9945.	68.80
290.0	66.65	10600.	71.10
298.15	68.42	11151.	72.98
300.0	68.84	11277.	73.40
310.0	71.10	11977.	75.69
320.0	73.42	12700.	77.99
330.0	75.81	13446.	80.28
340.0	78.28	14216.	82.58
350.0	80.83	15012.	84.89
360.0	83.46	15833.	87.20
370.0	86.18	16681.	89.53

^aThe 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 7. Heat capacity measurements of poly(methyl acrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Sochava and Trapeznikova (1965) [34]	1. Amorphous	50-210	Adiabatic (1%)	Table [49]
Lebedev and Rabinovich (1967) [42, 43]	2. Amorphous $\bar{M}_v = 162,000$	60-300	Adiabatic (0.5%)	Table
Hoffman and Knappe (1971) [46]	3. Copolymers ^a	80-440	Adiabatic (1%)	Graph
Shieman et al. (1972) [51]	4. Amorphous ^b	80-390	Adiabatic (0.5%)	80-250:Table ^b 300-390:Graph
Gaur and Wunderlich (1981) [7]	5. Amorphous	220-490	DSC ^c (1%)	Table

^aHeat capacity of poly(methyl acrylate-co-methyl methacrylate) extrapolated to zero content of methylmethacrylate.

^bHeat capacity data below the glass transition on a series poly(methyl acrylate-co-acrylonitrile) and poly(methyl acrylate-co-vinyl chloride) copolymers extrapolated to 100% methyl acrylate and averaged.

^cAverage of two measurements.

Table 8. Heat capacity measurements of poly(ethyl acrylate)

Investigator	Sample no., characterizations	Temperature range (K)	Experimental technique (claimed uncertainty).	Source of data
Hoffmann and Knappe (1971) [46]	6. Copolymers ^a	80-440	Adiabatic (1%)	Graph
Gaur and Wunderlich (1981) [7]	7. Amorphous $\bar{M}_w = 125,000$ $\bar{M}_n = 38,600$	220-490	DSC ^b (1%)	Table

^aHeat capacity of poly(ethylacrylate-co-methyl methacrylate) extrapolated to zero content methylmethacrylate.

^bAverage of two measurements.

Table 9. Heat capacity measurements of poly(n-butyl acrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Hoffmann and Knappe (1971) [46]	8. Amorphous	80-400	Adiabatic (1%)	Graph ^a
Gaur and Wunderlich (1981) [7]	9. Amorphous $\bar{M}_w = 119,000$ $\bar{M}_n = 33,000$	270-440	DSC ^b (1%)	Table

^aStraight line drawn through the heat capacity temperature plot to retrieve the data below T_g .

^bAverage of two measurements.

Table 10. Heat capacity measurements of poly(iso-butyl acrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Gaur and Wunderlich (1981) [7]	10. Amorphous $\bar{M}_w = 116,000$ $\bar{M}_n = 31,600$	220-500	DSC ^a (1%)	Table

^aAverage of two measurements.

Table 11. Heat capacity measurements of poly(octadecyl acrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Gaur and Wunderlich (1981) [7]	11. Amorphous $\bar{M}_w = 23,300$ $\bar{M}_n = 13,000$	230-490	DSC ^a (1%)	Table

^aAverage of five measurements

Table 12. Heat capacity measurements of poly(methacrylic acid)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Socheva and Trapeznikova (1965) [34]	12. Amorphous	50-210	Adiabatic (1%)	Table [49]
Rabinovich et al. (1967) [41]	13. Amorphous $\bar{M}_w = 560,000$	60-300	Adiabatic (0.5%)	Table

Table 13. Heat capacity measurements of poly(ethyl methacrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Hoffmann and Knappe (1971) [46]	27. Amorphous $M_w \approx 10^6$	80-400	Adiabatic (0.5%)	Graph ^a
Gaur and Wunderlich (1981) [7]	29. Amorphous $\bar{M}_w = 340,000$ $\bar{M}_n = 126,000$	230-380	DSC (1%)	Table ^b

^aStraight lines drawn through the heat capacity temperature plot to retrieve data.

^bAverage of two measurements.

Table 14. Heat capacity measurements of poly(n-butyl methacrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Hoffmann and Knappe (1971) [46]	30. $T_g = 286$ K	80-440	Adiabatic (1%)	Graph ^a
Gaur and Wunderlich (1981) [7]	32. Amorphous $\bar{M}_w = 320,000$ $\bar{M}_n = 73,500$	230-380	DSC ^b (1%)	Table

^aStraight line drawn through heat capacity - temperature plot to retrieve data.

^bAverage of three measurements.

Table 15. Heat capacity measurements of poly(iso-butyl methacrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Gaur and Wunderlich (1981) [7]	33. Amorphous $\bar{M}_w = 300,000$ $\bar{M}_n = 140,000$	230-400	DSC ^a (1%)	Table

^aAverage of two measurements.

Table 16. Heat capacity measurements of poly(hexyl methacrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lai (1976) [25]	34. AIBN initiated polymer $\bar{M}_n = 149,000$ $T_g = 268 \text{ K}$	300-420	DSC (Unreported)	Table

Table 17. Heat capacity measurements of poly(dodecyl methacrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Gaur and Wunderlich (1981) [7]	36. Amorphous $\bar{M}_w = 113,000$ $\bar{M}_n = 77,000$	270-400 ^a	DSC (1%) ^b	Table

^aData from 220-260 associated with side chain melting .^bAverage of two measurements .

Table 18. Heat capacity measurements of poly(octadecyl methacrylate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of Data
Gaur and Wunderlich (1981) [7]	37. Amorphous $\bar{M}_w = 671,000$ $\bar{M}_n = 97,200$	220-490	DSC (1%) ^a	Table

^aAverage of two measurements .

Table 19. Heat capacity measurements of polymethacrylamide

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lebedev and Rabinovich (1967) [42, 43]	40. Amorphous	60-300	Adiabatic (0.5%)	Table

Table 20. Recommended heat capacity data for glassy polyacrylates^a
 in J mol⁻¹K⁻¹

T(K)	PMA	PEA	PNBA	PIBA
10	0.4563			
20	4.642			
30	11.70			
40	19.35			
50	26.57			
60	33.08			
70	38.89			
80	44.07		71.75	
90	48.73	58.00	78.20	
100	52.97	62.51	84.65	
110	56.87	66.84	91.11	
120	60.49	71.06	97.56	
130	63.89	75.20	104.0	
140	67.12	79.28	110.5	
150	70.21	83.32	116.9	
160	73.19	87.33	123.4	
170	76.09	91.31	129.8	
180	78.93	95.26	136.3	
190	81.72	99.21	142.7	
200	84.49	103.1	149.2	
210	87.23	107.1	155.6	
220	89.96	111.0		155.8
230	92.69	114.9		163.5
240	95.43	118.8		171.3
250	98.18			
260	100.9			
270	103.7			

^aThe table 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 21. Recommended heat capacity data for molten
polyacrylates^a in J mol⁻¹K⁻¹

T(K)	PMA	PEA	PNBA	PIBA	PODA
220			206.9		
230			210.2		
240			213.5		
250		168.1	216.8	215.2	
260		170.2	220.1	218.6	
270		172.4	223.4	221.9	
280	148.7	174.6	226.7	225.3	
290	150.4	176.7	230.0	228.7	
300	152.0	178.9	233.3	232.1	
310	153.6	181.1	236.6	235.5	
320	155.2	183.2	239.9	238.9	
330	156.9	185.4	243.2	242.2	
340	158.5	187.6	246.5	245.6	692.1
350	160.1	189.7	249.8	249.0	701.5
360	161.7	191.9	253.1	252.4	711.0
370	163.4	194.0	256.4	255.8	720.4
380	165.0	196.2	259.7	259.2	729.9
390	166.6	198.4	263.0	262.5	739.4
400	168.2	200.5	266.3	265.9	748.8
410	169.9	202.7	269.5	269.3	758.3
420	171.5	204.9	272.8	272.7	767.8
430	173.1	207.0	276.1	276.1	777.2
440	174.7	209.2	279.4	279.5	786.7
450	176.4	211.4		282.8	796.2
460	178.0	213.5		286.2	805.6
470	179.6	215.7		289.6	815.1
480	181.2	217.9		293.0	824.5
490	182.9	220.0		296.4	834.0
500	184.5	222.2		299.8	843.5

^aThe table 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 22. Recommended heat capacity data for glassy
 polymethacrylates^a in J mol⁻¹K⁻¹

T(K)	PMAA	PEMA	PNBMA	PIBMA	PMAM
10	1.231				0.2127
20	5.495				2.811
30	10.85				8.136
40	16.38				14.70
50	21.76				21.50
60	26.90				28.07
70	31.80				34.25
80	36.46	58.84	77.81		39.99
90	40.91	63.59	84.86		45.31
100	45.18	68.42	91.97		50.25
110	49.27	73.28	99.13		54.86
120	53.23	78.17	106.3		59.20
130	57.06	83.08	113.5		63.29
140	60.77	88.00	120.8		67.18
150	64.39	92.94	128.0		70.90
160	67.93	97.88	135.3		74.48
170	71.39	102.8	142.5		77.94
180	74.78	107.8	149.8		81.30
190	78.12	112.7	157.1		84.59
200	81.41	117.7	164.4		87.81
210	84.65	122.7	171.6		90.98
220	87.85	127.6	178.9		94.11
230	91.02	132.6	186.2	173.9	97.21
240	94.16	137.6	193.5	181.0	100.3
250	97.27	142.5	200.8	188.0	103.3
260	100.4	147.5	208.1	195.1	106.4
270	103.4	152.5	215.3	202.2	109.5
280	106.5	157.5	222.6	209.2	112.5
290	109.5	162.4	229.9	216.3	115.6
300	112.5	167.4		223.4	118.7
310		172.4		230.4	
320		177.4		237.5	
330		182.3			

^aThe 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 23. Recommended heat capacity data for molten
polymethacrylates^a in $\text{J mol}^{-1} \text{K}^{-1}$

T(K)	PEMA	PNBMA	PIBMA	PHMA	PDDMA	PODMA
240					469.9	
250					477.0	
260					484.2	
270				310.8	491.3	
280				315.4	498.5	
290				320.1	505.6	
300		263.4		324.8	512.8	
310		268.3		329.5	520.0	
320		273.2		334.2	527.1	702.5
330		278.1	281.8	338.9	534.3	713.8
340	218.8	282.9	284.4	343.6	541.4	725.1
350	222.5	287.8	287.1	348.2	548.6	736.4
360	226.2	292.7	289.8	352.9	555.7	747.7
370	229.9	297.6	292.4	357.6	562.9	759.1
380	233.6	302.5	295.1	362.3	570.0	770.4
390		307.3	297.7	367.0	577.2	781.7
400		312.2	300.4	371.7	584.4	793.0
410		317.1		376.4		804.4
420		322.0		381.0		815.7
430		326.9				827.0
440		331.7				838.3
450		336.6				849.6
460						861.0
470						872.3
480						883.6
490						894.9
500						906.2

^aThe table 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 24. Results of curve fitting literature data on heat capacity of acrylic polymers to derive recommended data.

Polymer	State	Equation ^a	Temperature range (K) ^b	RMS dev. (%)	No. of data points	Data points not included sample no. (Temp.)
PMA	Glassy	I	10-279	1.1	60	1 (50-210)
	Molten	II	279-500	0.5	21	2,3,4 ^c
PEA	Glassy	III	90-249	0.5	15	7 (220-240)
	Molten	IV	249-500	0.3	24	6 (270-370)
PNBA	Glassy	V ^d	80-219			
	Molten	VI	219-440	0.4	46	
PIBA	Glassy	VII	220-249	0.2	3	
	Molten	VIII	249-500	0.5	24	
PODA	Molten	IX	332-500	0.4	17	
PMAA	Glassy	X	60-300	0.5	25	12 (50-210)
PEMA	Glassy	XI	80-338	0.3	35	
	Molten	XII	338-380	0.0	3	27 (360-400)
PNBMA	Glassy	XIII	80-293	0.5	25	
	Molten	XIV	293-450	0.6	31	
PIBMA	Glassy	XV	230-326	0.4	7	
	Molten	XVI	326-400	0.5	6	
PHMA	Molten	XVII ^e	279-420			
PDDMA	Molten	XVIII	240-400	0.5	14	
PODMA	Molten	XIX	320-500	0.6	18	
PMAM	Glassy	XX	60-300	0.9	25	

^aEquations are listed separately in table 25.^bThe temperature range over which the equation is valid.^cData discarded over the entire temperature range.^dStraight line drawn through authors' graphical data^eAuthors' curve fitted data.

Table 25. Equations cited in table 24

Equation	I	$C_p = \exp[0.14416(\ln T)^3 - 2.22407(\ln T)^2 + 12.078(\ln T) - 18.5634] \text{ J mol}^{-1}\text{K}^{-1}$
Equation	II	$C_p = 0.1625 T + 103.24 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	III	$C_p = -2.76712 \cdot 10^4 T^{-2} + 0.38556T + 25.71 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	IV	$C_p = 0.2164 T + 113.96 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	V	$C_p = 0.6452 T + 20.13 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	VI	$C_p = 0.3298 T + 134.34 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	VII	$C_p = 0.775 T - 14.75 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	VIII	$C_p = 0.3384 T + 130.57 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	IX	$C_p = 0.9464 T + 370.29 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	X	$C_p = \exp[0.0566117(\ln T)^3 - 0.929753(\ln T)^2 + 5.88628(\ln T) - 9.10792] \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XI	$C_p = 6.7667 \cdot 10^3 T^{-2} + 0.498 T + 17.94 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XII	$C_p = 0.37 T + 92.97 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XIII	$C_p = 7.7382 \cdot 10^3 T^{-2} + 0.7296 T + 18.23 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XIV	$C_p = 0.4881 T + 116.98 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XV	$C_p = 0.7064 T + 11.43 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XVI	$C_p = 0.2666 T + 193.79 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XVII	$C_p = 0.4686 T + 184.25 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XVIII	$C_p = 0.7155 T + 298.14 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XIX	$C_p = 1.132 T + 340.2 \text{ J mol}^{-1}\text{K}^{-1}$
Equation	XX	$C_p = \exp[0.137146(\ln T)^3 - 2.19746(\ln T)^2 + 12.463(\ln T) - 20.02684] \text{ J mol}^{-1}\text{K}^{-1}$

entire temperature range. The data on sample 7 (PEA) from 220 to 240 K were also omitted. These data are the first four data points of DSC measurements through the glass transition and differ from more reliable data by 5%.

In the molten state, DSC measurements are considered more reliable (see ref. [1]) than adiabatic measurements. The adiabatic measurements on molten samples (sample nos. 2, 3, 4, 6, and 27) showing deviations (2–5%) from DSC data from our laboratory were omitted.

The recommended data on poly(methyl acrylate), poly(methacrylic acid) and polymethacrylamide were obtained from curve fitted functions reported in the literature

$$\text{PMA [42, 43]} \quad C_p = 3 \left\{ D_1 \left(\frac{420}{T} \right) - \frac{123}{420} \right.$$

$$\left. \times \left[D_1 \left(\frac{123}{T} \right) - D_3 \left(\frac{123}{T} \right) \right] \right\} \quad (7)$$

$$\text{PMAA [41]} \quad C_p = 2.5 \left\{ D_1 \left(\frac{357}{T} \right) - \frac{214}{357} \right. \\ \left. \times \left[D_1 \left(\frac{214}{T} \right) - D_3 \left(\frac{214}{T} \right) \right] \right\} \quad (8)$$

$$\text{PMAM [42, 43]} \quad C_p = 13.5 D_3 \left(\frac{390}{T} \right) \\ + E \left(\frac{504}{T} \right) + 10E \left(\frac{700}{T} \right) \quad (9)$$

D_1 , D_3 , and E refer to one dimensional Debye, three dimensional Debye and Einstein functions, respectively. These data are also listed in tables 21 and 23.

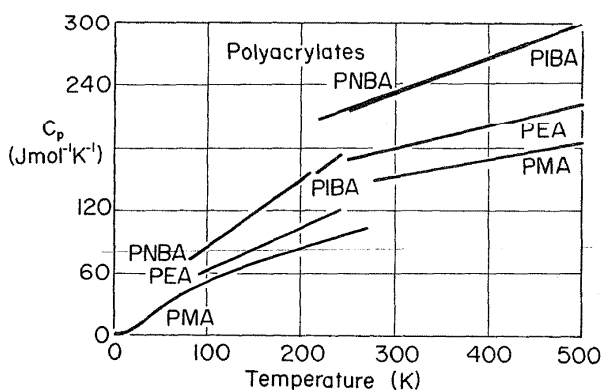


FIGURE 1: Recommended data on heat capacity of polyacrylates.

PMA: Poly(methyl acrylate)
PEA: Poly(ethyl acrylate)
PNBA: Poly(n-butyl acrylate)
PIBA: Poly(iso-butyl acrylate)

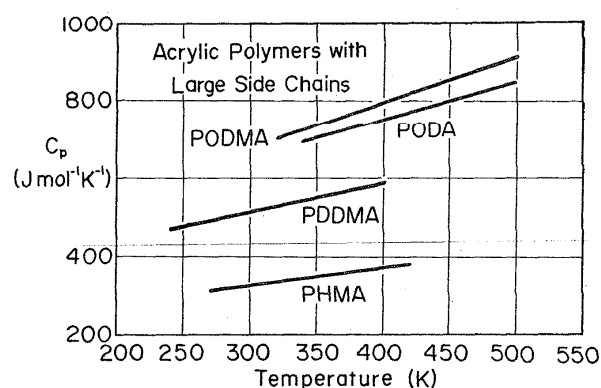


FIGURE 3: Recommended data on heat capacity of acrylic polymers with large side groups.

PHMA: Poly(hexyl methacrylate)
PDDMA: Poly(dodecyl methacrylate)
PODA: Poly(octadecyl acrylate)
PODMA: Poly(octadecyl methacrylate)

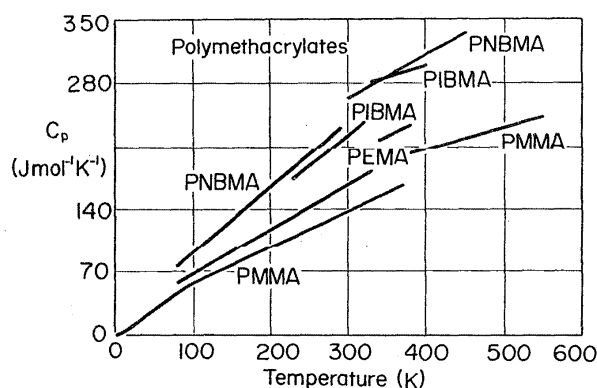


FIGURE 2: Recommended data on heat capacity of polymethacrylates.

PMMA: Poly(methyl methacrylate)
PEMA: Poly(ethyl methacrylate)
PNBMA: Poly(n-butyl methacrylate)
PIBMA: Poly(iso-butyl methacrylate)

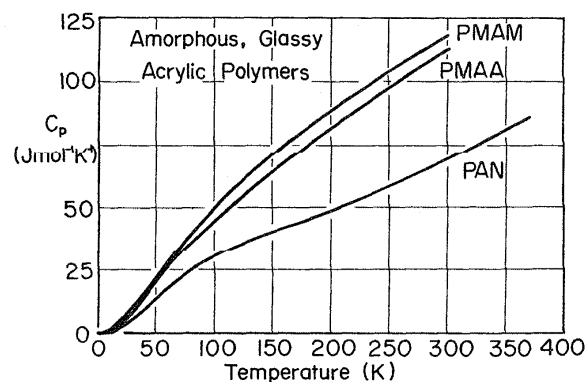


FIGURE 4: Recommended heat capacity data for polyacrylonitrile (PAN), poly(methacrylic acid) (PMAA) and polymethacrylamide (PMAM).

3. Conclusions

Heat capacities of poly(methyl methacrylate), polyacrylonitrile, poly(methyl acrylate), poly(ethyl acrylate), poly(n-butyl acrylate), poly(iso-butyl acrylate), poly(octadecyl acrylate), poly(methacrylic acid), poly(ethyl methacrylate), poly(n-butyl methacrylate), poly(iso-butyl methacrylate), poly(hexyl methacrylate), poly(dodecyl methacrylate), poly(octadecyl methacrylate) and polymethacrylamide are reviewed on the basis of measurements on 35 samples reported in the literature. A set of recommended data is derived for each acrylic polymer in their amorphous state. These data are plotted in figures 1 to 4. Entropy and enthalpy functions have been derived for poly(methyl methacrylate) and polyacrylonitrile.

Recommended heat capacity data on these acrylic polymers are being analyzed in terms of their chemical structure,

to derive heat capacities of various structural units towards an updated heat capacity addition scheme [53–55]. The results of this analysis would be reported at a later date.

Heat capacity change of the glass transitions for acrylic polymers for which recommended heat capacity data are available in their glassy and molten states are listed in table 26. These $\Delta C_p(T_g)$ data are being analyzed, along with $\Delta C_p(T_g)$ data for other linear macromolecules in terms of the hole theory of the glass transition [54, 56]. The results of this analysis will also be reported at a later date.

Acknowledgments

This work has been supported by the National Science Foundation Grant #DMR78-15279, Polymers Program.

Table 26. Heat capacity change at the glass transition temperature

Polymer	T_g (K)	ΔC_p ($J\ mol^{-1}\ K^{-1}$)
Poly(methyl acrylate)	279	42.3
Poly(ethyl acrylate)	249	45.6
Poly(n-butyl acrylate)	218	45.4
Poly(iso-butyl acrylate)	249	36.6
Poly(methyl methacrylate)	378	33.5
Poly(ethyl methacrylate)	338	31.7
Poly(n-butyl methacrylate)	293	29.7
Poly(iso-butyl methacrylate)	326	39.0

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