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Calorimetric Behavior of Methacrylic Polymers

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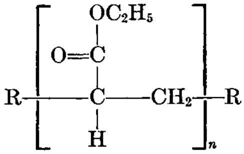
Synopsis

Specific heats for poly(methyl methacrylate), poly(diethylaminoethyl methacrylate), poly(cyclohexyl methacrylate), poly(allyl methacrylate), and poly(ethyl acrylate) were measured from 120 to 300°C. with a drop calorimeter. It was found that existing solid-state theories and equations were unable to correlate the data. The reason advanced was that such theories were developed for crystalline materials, which differed greatly from the amorphous polymers of the present work. A more successful approach was to use a correlation technique originally developed for organic liquids.

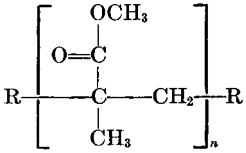
Polymers are one of the most important of all engineering materials, but in spite of their importance little is known about their physical and chemical properties. This is particularly true of the calorimetric behavior of polymers.

The present work was undertaken to help fill the need for calorimetric data. The study determined experimental enthalpies for a group of methacrylic polymers: poly(methyl methacrylate), poly(dimethylaminoethyl methacrylate), poly(allyl methacrylate), poly(cyclohexyl methacrylate), and an acrylic polymer, poly(ethyl acrylate). The accompanying schemes show the structures of their polymer repeating units. Correlation techniques for the polymers' specific heats were developed; they are based on the structural characteristics of the polymers.



$$\mathrm{R}-\left[\begin{array}{c} \mathrm{OC_2H_5} \\ | \\ \mathrm{O{=}C} \\ | \\ -\mathrm{C}-\mathrm{CH_2}- \\ | \\ \mathrm{H} \end{array}\right]_n-\mathrm{R}$$

poly(ethyl acrylate)



$$\mathrm{R}-\left[\begin{array}{c} \mathrm{OCH_3} \\ | \\ \mathrm{O{=}C} \\ | \\ -\mathrm{C}-\mathrm{CH_2}- \\ | \\ \mathrm{CH_3} \end{array}\right]_n-\mathrm{R}$$

poly(methyl methacrylate)

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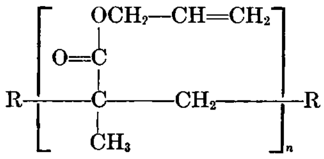
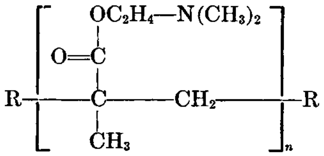
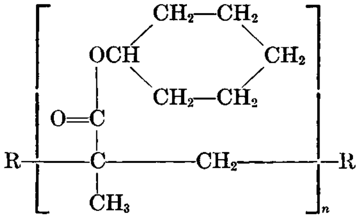


poly(allyl methacrylate)



poly(dimethylaminoethyl methacrylate)



poly(cyclohexyl methacrylate)

The experimental work was carried out with a drop calorimeter (Fig. 1). The device was based on the earlier designs of Southard[1] and Ginnings and Corruccini.[2] The calorimeter consisted of four basic units: a constant-temperature bath, drop chute and drop mechanism, the adiabatic calorimeter, and the temperature-measuring system.

The polymer samples used in this work were prepared by bulk polymerizations. These were carried out in test tubes with benzoyl peroxide as catalyst. Two stages were used. The first involved placing test tubes containing monomer and catalyst into a stirred bath at 80°C. The reaction was carried out until the sample had solidified. The solid samples were then placed in a nitrogen bleed oven at 160°C. overnight. The finished polymers were cut into cylindrical samples for use in the calorimeter.

The samples, prepared as described above, were placed in the sample capsule. The capsule and its contents were then positioned in the drop chute by means of the drop wire. When this was done, the drop chute, sample, and capsule were surrounded by the constant-temperature bath. Water was admitted to the coil on the portion of the drop tube below the bath, and the radiation shields were positioned. The bath heaters and stirrers were turned on, and the bath was brought to its desired temperature level. Nitrogen was continually bled around the sample during heating, to prevent degradation. As the bath was reaching the desired temperature, the capsule receiver was attached to the bottom of the drop tube, and the calorimeter was filled with distilled water.

The temperature of the bath surrounding the sample was kept to within ±0.5°C. of the desired level. When the bath temperature had been constant for 1 hr. it was assumed that the sample and capsule were also at

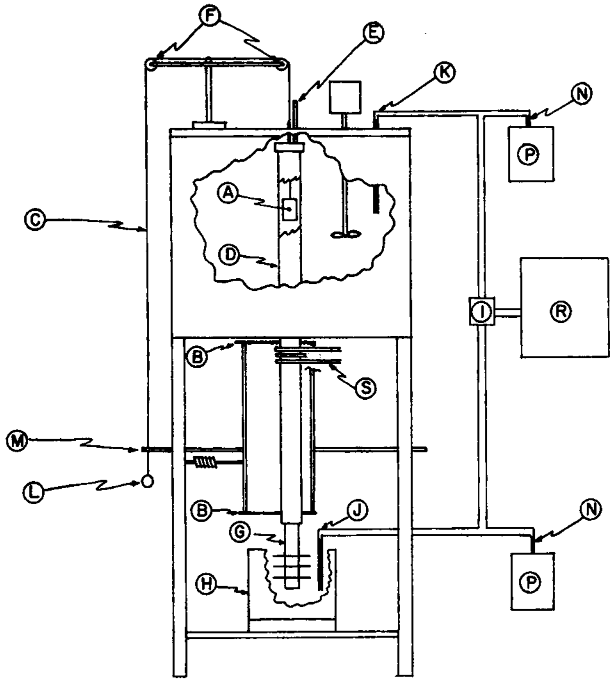


Fig. 1. Schematic of drop calorimeter: (*A*) sample capsule; (*B*) radiation shields; (*C*) drop wire; (*D*) drop tube; (*E*) nitrogen inlet; (*F*) pulleys; (*G*) capsule receiver, (*H*) calorimeter; (*I*) two-way switch; (*J*) calorimeter thermopile; (*K*) oil-bath thermopile; (*L*) capsule counterweight; (*M*) shield lever; (*N*) reference thermopiles; (*P*) ice-water baths; (*R*) recorder; (*S*) cooling-water coil.

the desired temperature. Temperature readings were also taken for the calorimeter. When no detectable change in the water had taken place, the drop was made. This was done by removing the radiation shields and releasing the free end of the drop wire. When the capsule was in the receiver, the radiation shields were replaced. The temperature was recorded continuously, until it had reached a constant value.

The procedure was repeated for the drop of the empty capsule and the

TABLE I
Polymer Specific Heats

	Specific heats at temperature (°C.), cal./g.-°C.						
Polymer	120	150	180	210	240	270	300
Poly(methyl methacrylate)	0.66	0.75	0.80	0.89	1.12	1.54	2.52
Poly(dimethylaminoethyl methacrylate)	0.40	0.42	0.53	0.72	0.93	1.47	2.36
Poly(cyclohexyl methacrylate)	0.31	0.33	0.44	0.59	0.76	1.14	2.21
Poly(allyl methacrylate)	0.19	0.28	0.41	0.56	0.83	1.14	1.58
Poly(ethyl acrylate)	0.17	0.21	0.32	0.41	0.48	0.54	0.63

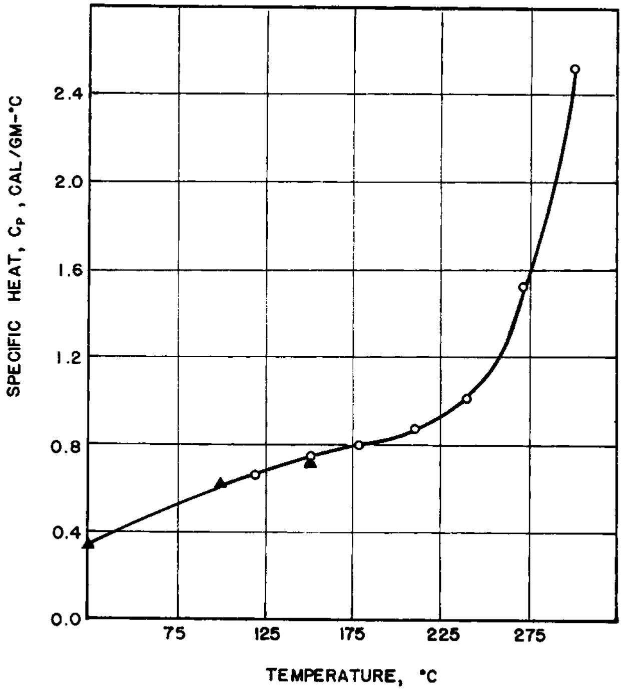


Fig. 2. Specific heat of poly(methyl methacrylate) vs. temperature: (▲) from Bernhardt,[7] (○) present work.

capsule containing a known weight of a characterized silica. All these data permitted the calculation of the polymer enthalpies.

The specific heats of the various polymers are summarized in Table I and Figures 2–5. No literature data were found for any of the polymers except poly(methyl methacrylate). Four investigations reported, those of Dainton et al.,[3] Warfield and Petree,[4] Sochava,[5] and Sochava and Trapeznikova,[6] had considered specific-heat behavior up to only 13°C. The only data for the same temperature range as that of the present study were some reported by Bernhardt.[7] They are compared with those of the present work in Figure 2. As may be seen, there is good agreement between both sets of data.

It may be seen in Figure 3 that the data for poly(methyl methacrylate), poly(dimethylaminoethyl methacrylate), and poly(cyclohexyl methacrylate) form a family of curves. The curves seem to be related to mer weight, since poly(methyl methacrylate), which has the lowest mer weight, has a curve that lies above that of poly(dimethylaminoethyl methacrylate), which has an intermediate mer weight, and its curve in turn lies above that of poly(cyclohexyl methacrylate), which has a still higher mer weight. On the other hand, the data for poly(allyl methacrylate) behaves in a somewhat different manner. In Figure 4 these data are compared with those for poly(dimethylaminoethyl methacrylate), which has a higher mer weight

(157 versus 126). As may be seen, the behavior shown in Figure 3 is contradicted. Furthermore, the curve for poly(allyl methacrylate) actually overlaps that for poly(cyclohexyl methacrylate), which also has a higher mer weight. The probable reason for the different behavior of the poly(allyl methacrylate) is that it could crosslink during polymerization; this would produce a structure quite different from the linear polymers poly(methyl methacrylate), poly(dimethylaminoethyl methacrylate), and poly(cyclohexyl methacrylate).

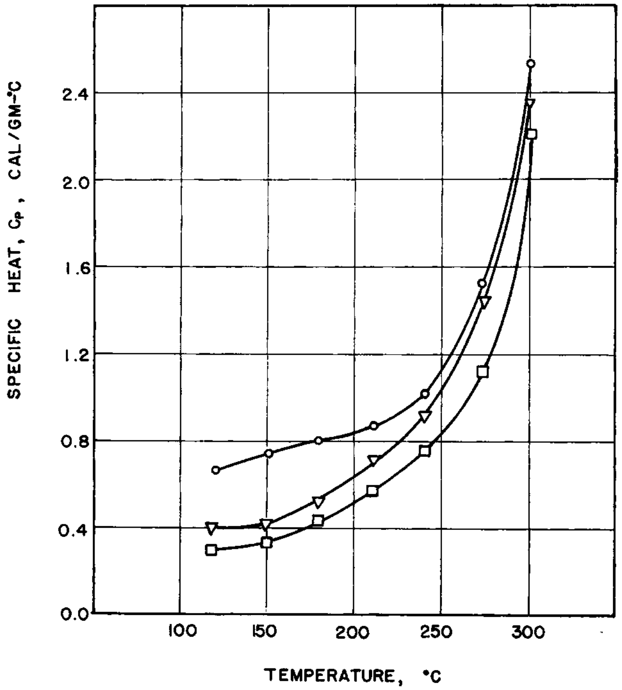


Fig. 3. Specific heats of (○) poly(methyl methacrylate); (▽) poly(dimethylaminoethyl methacrylate); (□) poly(cyclohexyl methacrylate) vs. temperature.

Data for poly(ethyl acrylate) are shown in Figure 5. They are not the same as those for poly(methyl methacrylate), even though the mer weights are the same. The difference in behavior is probably due to basic structural differences (see the structural formulas).

Equations and correlations for solid specific-heat behavior generally apply to crystalline materials. Because of this difficulties were encountered in attempts at correlating the data of the present work, the polymers studied being mainly amorphous. Attempts at treating the polymers as Einstein or Debye solids failed completely. Semiempirical equations such as Kopp's rule[8] were also unable to predict the behavior of the polymers studied. The usual solid-state equations or correlations apparently apply only to semicrystalline polymers,[9] such as polyethylene, at low tempera-

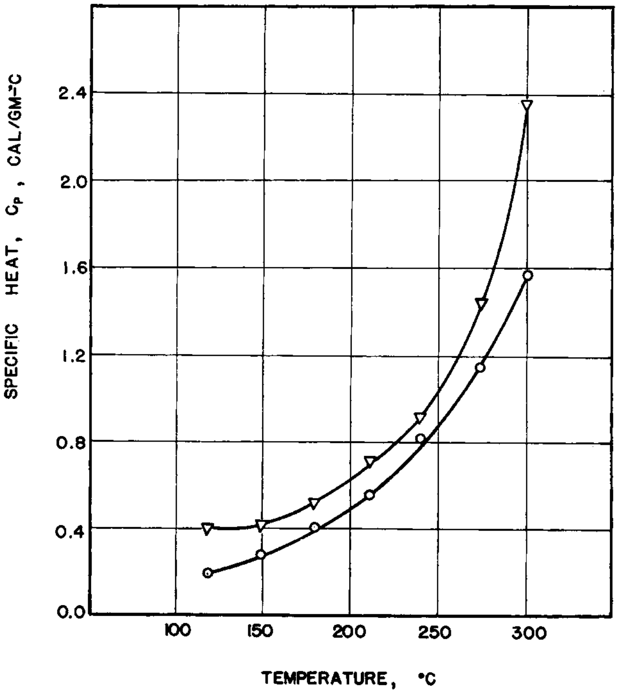


Fig. 4. Specific heats of (△) poly(dimethylaminoethyl methacrylate) and (○) poly(allyl methacrylate) vs. temperature.

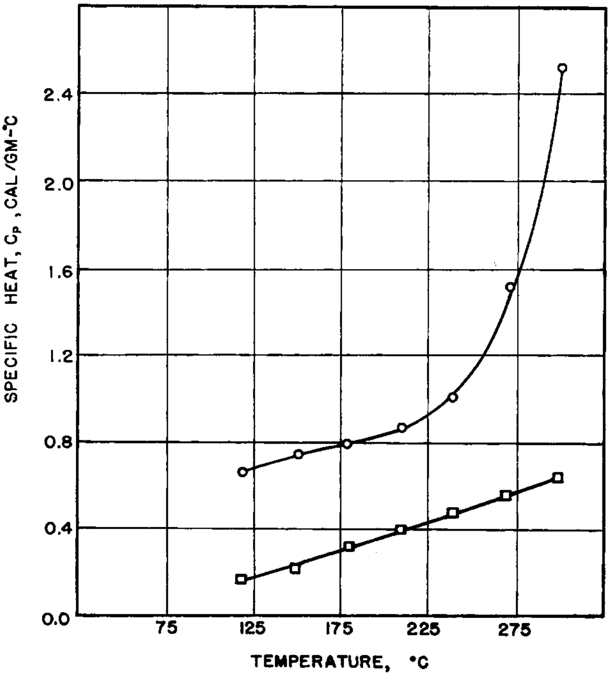


Fig. 5. Specific heats of (○) poly(methyl methacrylate) and (□) poly(ethyl acrylate) vs. temperature.

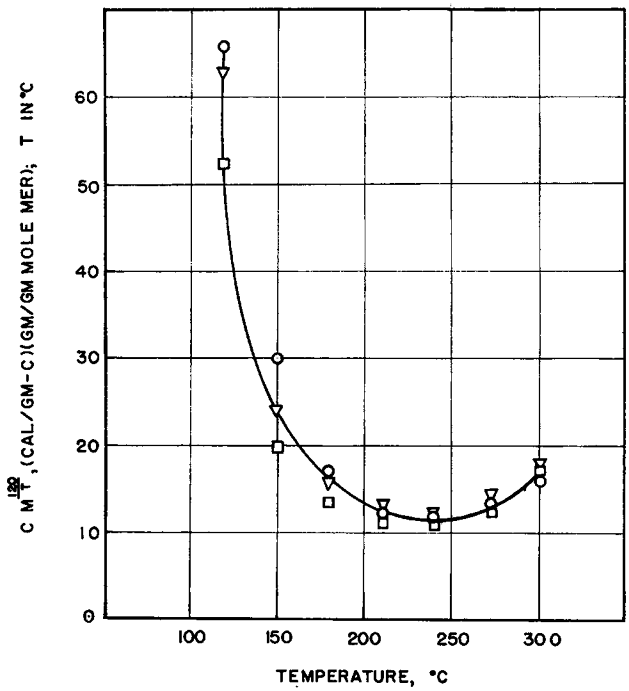


Fig. 6. Correlation of specific heats of linear methacrylic polymers, $C_pM^{120/T}$ vs. temperature: (○) poly(methyl methacrylate; (▽) poly(dimethylaminoethyl methacrylate); (□) poly(cyclohexyl methacrylate).

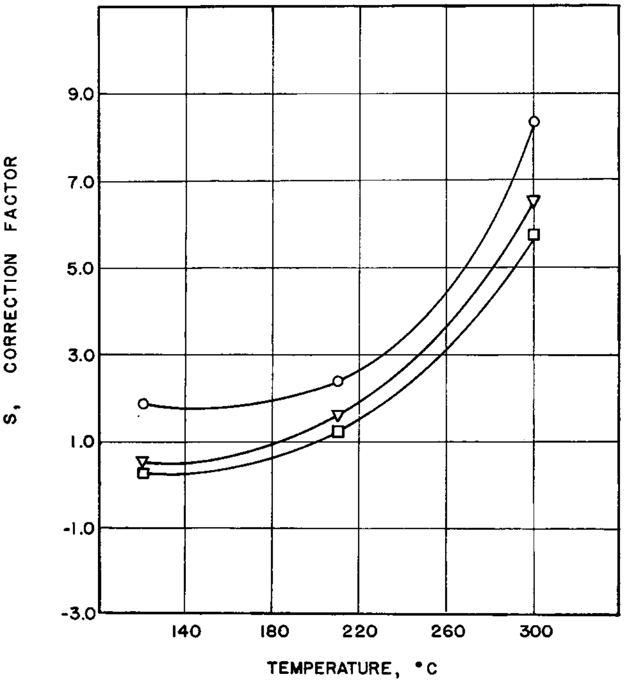


Fig. 7. Heat capacity correction factors S vs. temperature for linear methacrylic polymers: (○) poly(methyl methacrylate; (▽) poly(dimethylaminoethyl methacrylate); (□) poly(cyclohexyl methacrylate).

tures (100°K. or less). For systems that are mainly amorphous in nature other techniques had to be devised.

One approach that may be taken is the empirical one. Figure 6 is a plot of $C_pM^{120/T}$ versus temperature for the linear methacrylic polymers.

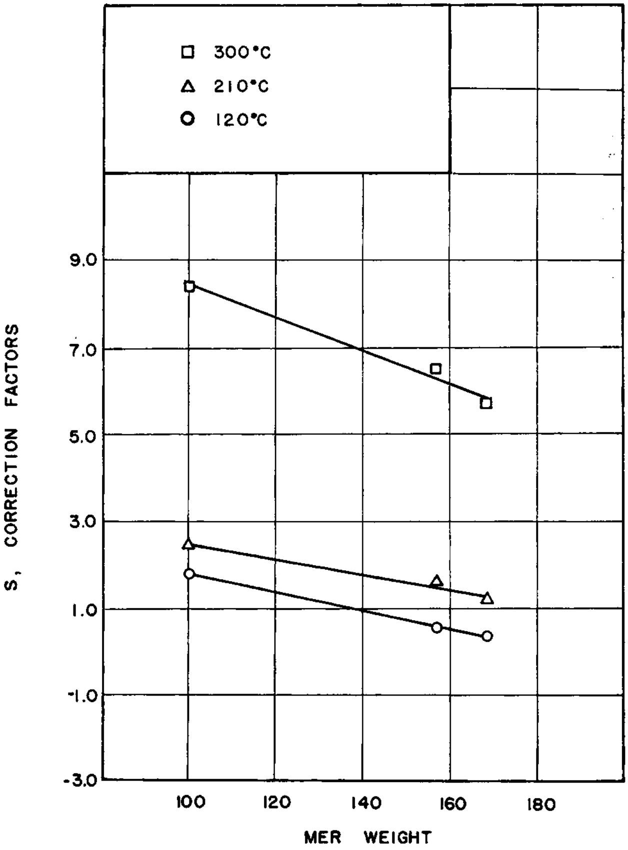


Fig. 8. Heat capacity correction factors S vs. mer weight for linear methacrylic polymers at temperatures, °C.: (□) 300; (△) 210; (○) 120.

Here M is the polymer mer weight, and T is the temperature in degrees centigrade. The correlation indicates that

$$C_p = \phi(\text{mer weight, temperature})$$

and that specific heat has a lesser dependence on mer weight at higher temperatures.

The failure of existing solid specific-heat theories to describe the behavior of the amorphous polymers used in this study led to the idea that perhaps correlations for organic liquids might prove more effective. This approach was felt to be reasonable because the structure of the amorphous polymers might resemble more closely organic liquids than crystalline solids. A number of such correlations based upon structural considerations had been developed. These included the studies of Sakiadis and Coates[10] and of Johnson and Huang,[11] both of which were cited by Reid and Sherwood[12] as recommended correlations for organic liquids. The method of Johnson and Huang[11] was based on the addition of atomic-group heat capacities, while that of Sakiadis and Coates[10] involved an equation based on statistical mechanics:

$$C = (6 + a)R + \sum q_i C_{\omega i} + \frac{(3n - 6 - a - \sum q_i)\, S \sum q_i C_{\delta i}}{\sum q_i}$$

where C = heat capacity (cal./g.-mole-°K.), a = number of freely rotating bonds, q_i = number of valence bonds of ith type, n = number of atoms in molecule, $C_{\omega i}$ and $C_{\delta i}$ = Einstein functions for stretching and deformation, R = gas constant (cal./g. mole-°K.), and S = factor, a function of molecular weight and type of compound.

The foregoing correlations and a modification of Kopp's rule for liquids, as developed by Gambrill,[13] were applied to the materials used in the present study. This was done by treating the characteristic mers of each of the polymers as organic molecules. The results again gave large errors, the best results being those with the correlation of Sakiadis and Coates.[10]

This suggested that a modification of this correlation could be used for amorphous polymers. The most likely item that could be modified was the S factor, since Sakiadis and Coates gave four different curves of S versus molecular weight for various types of organic liquids (i.e., aliphatic, aromatic, etc.). The S values for the linear methacrylic polymers were calculated and plotted as in Figures 7 and 8. When the S values from these curves were used in the correlation of Sakiadis and Coates, they yielded specific heats that deviated, on the average, 6% from the experimental data for poly(methyl methacrylate), poly(dimethylaminoethyl methacrylate), and poly(cyclohexyl methacrylate).

It should be noted that S was originally proposed as being a function only of structure and not of temperature. It is not surprising, however, that temperature also should be a factor in the S correlation, since there is still a considerable structural difference between an organic liquid made up of small molecules and an amorphous polymer made up of giant, intertwined molecules.

The S factor values were also determined for poly(ethyl acrylate); these were −0.56, 0.43, and 1.03 at 120, 210, and 300°C., respectively. It is suggested that they might be used for locating the endpoints of curves of S versus mer weight for acrylate polymers, as in Figure 8. Such curves might be parallel to those for the linear methacrylates and be used for deriving S values for estimating specific heats for acrylates of higher mer weights. Any such estimations would, of course, be quite rough, but at least they might furnish reasonable estimates for engineering calculations.

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