Heat of Polymerization of Chloroprene

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Determinations of the heat of polymerization are of great importance in connection with the study of polymerization reactions. Several methods have been used for this purpose during recent years. In a series of papers Tong and Kenyon [1-5] have described an isothermal calorimeter and the use of this on monomers of the vinyl type. Goldfinger, Josefowitz and Mark [6] and Evans and Tyrrall [7] have used adiabatic calorimeters. Roberts, Walton and Jessup [8] have determined heats of polymerization from heats of combustion, a method used previously by many investigators. Most of the measurements have been done on monomers of the vinyl type and some on butadiene and isoprene. As far as the present authors know only one value of the heat of polymerization of chloroprene (2-chloro-1,3-butadiene) has been published. Thus Walter [9] for polymerization in sodium oleate emulsion at 30° C gives the value 15.1 ± 0.8 kcal/monomer unit. No details about the measurements are given.

In this investigation the heat of polymerization of chloroprene has been measured at different initiator concentrations. An isothermal calorimeter of a construction very similar to that of Tong and Kenyon [1, 2] has been used. The polymerization has been made in bulk. Measurements have also been made on methyl methacrylate and styrene mainly in order to check the calorimeter.

EXPERIMENTAL

Description of calorimeter

The main difficulty in constructing the calorimeter was to achieve sufficient stability for long time runs. The time of polymerization of chloroprene can be as long as 15—20 hours. The calorimeter is shown in Fig. 1. By means of a ground joint flask (A) is connected to a double walled, cylindrical part (B).
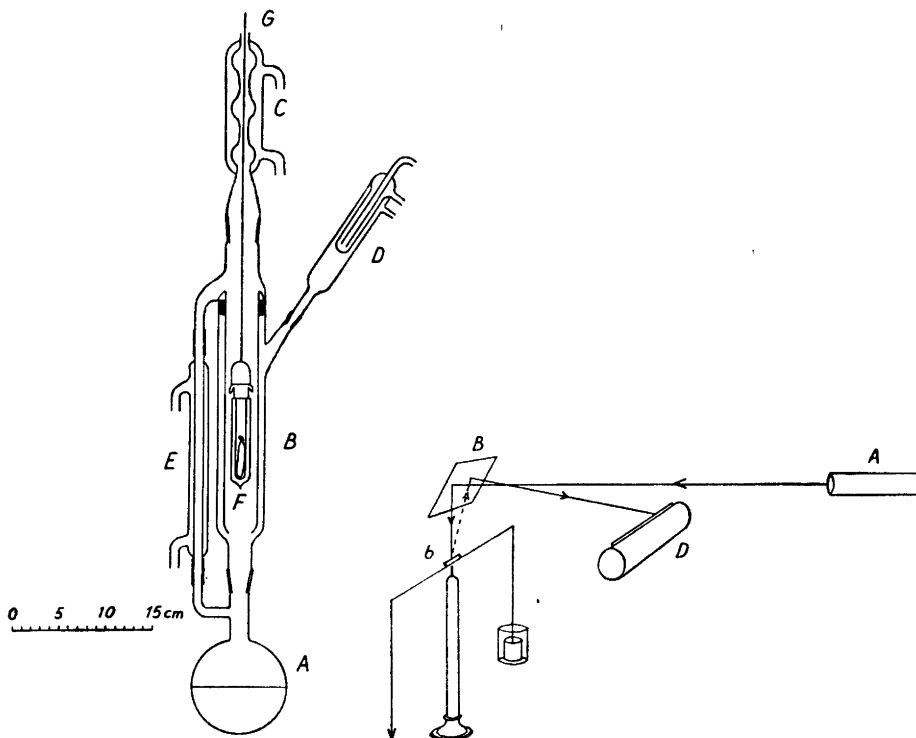
Fig. 1. Isothermal calorimeter.

Fig. 2. Selfrecording arrangement.

To the outer jacket of (B) a condenser (D) is attached. The inner jacket is connected through a side tube and the condenser (E) to flask (A). At the opening for the side tube a trap is made in which the condensate from condenser (C) is caught. The inner jacket is fixed to the outer one by means of thin cork strips and gelatine acetic acid cement. Inside the inner jacket a dewar tube is suspended freely from one of the arms of a balance by means of a thin metal wire (G). This tube has a capacity of about 60 ml. For long polymerization runs it is necessary to diminish the heat losses from the liquid in the dewar tube as much as possible, for which reason the innerwalls are silverplated *. The reaction tubes containing monomer are placed in the dewar vessel. In order to save time the heat exchange liquid in (F) is heated to the boiling point by means of a small electric heater submerged in the liquid, or the tube (F) is filled with the boiling liquid.

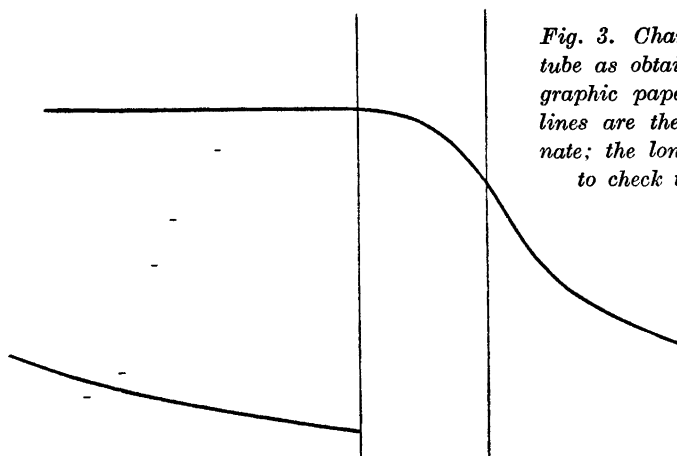* The dewar vessel was constructed by A. B. Lumalampan, Stockholm.

Fig. 3. Change in weight of the dewar tube as obtained directly on the photographic paper. The short, horizontal lines are the calibrations of the ordinate; the long, vertical lines are used to check the speed of the drum.

The selfrecording system shown in Fig. 2 is almost identical with that used by Tong and Kenyon [2]. The light beam from the thin filament of lamp (A) is reflected from mirror (B) to lens (b) (focal distance 1 m) attached to the midpoint of the beam of the balance. The lens is silverplated on the back side and hence reflects the light back to mirror (B) and to drum (D) which can be rotated at different speeds with a synchronous motor and a gear. A similar drum has been used by Andersson, Ställberg-Stenhagen and Stenhagen [10] and Claesson [11] for other purposes. By means of the lens (b) a sharp image of the filament is formed on the slit-shaped opening of the drum. A damping arrangement is attached to one of the arms of the balance. It consists of a glass cup, containing tare weights placed in a larger cup containing a zinc chloride solution of a suitable density. A thin layer of paraffin oil prevents evaporation of water from the zinc chloride solution. During a run a curve is obtained on photographic paper placed in the drum. The ordinate will be proportional to the change in weight of the dewar tube; the abscissa gives the time. In order to check the speed of rotation and to correct for shrinking of the photographic paper the slit is illuminated at definite time intervals. The ordinate is calibrated by means of known weights placed on the balance. An example of such a curve is given in Fig. 3. From these curves the relationship between the heat evolved during the polymerization and the time is easily obtained.

Purification of monomers

Chloroprene. This was obtained from large scale production in plant. There it had been washed with acid sodium sulfite to remove aldehydes, distil-
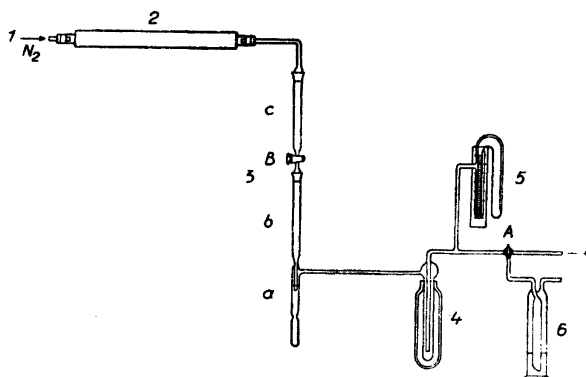
Fig. 4. Arrangement for filling the reaction tubes.

led in a column and stabilized with thiodiphenylamine. This chloroprene still contains water, peroxides and dissolved oxygen. For further purification it was stored some time over calcium chloride and then distilled at atmospheric pressure in a bead packed column with about eight theoretical plates. Some calcium carbonate was added in order to neutralize small amounts of hydrochloric acid split off during heating. The distillate was stabilized with thiodiphenylamine and stored over sodium sulfate. The quantity necessary for each run in the calorimeter was then distilled at atmospheric pressure in a wire-gauze column with about 35 theoretical plates. Carbon dioxide was passed through the column and the receiver was cooled with dry ice. All these precautions were taken in order to prevent, as far as possible, the formation of polymers and peroxides in the monomer.

Methyl methacrylate. This was distilled in the bead packed column at reduced pressure and then stored in a closed bottle at — 15° C.

Styrene. This was distilled in the bead packed column at reduced pressure and then immediately used.

Filling of the reaction tubes

Peroxides formed by reaction of the monomers and oxygen in the air influence the course of the polymerization. Therefore, special precautions were taken to prevent the monomers from being in contact with the air during the filling of the reaction tubes. The arrangement shown in Fig. 4 was used for this purpose. Nitrogen was introduced into the system at (1) and freed from oxygen in the copper oven (2), consisting of a glass tube filled to 50 cm of its

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length with very small pieces of reduced copper. According to Meyer[12] such an oven is effective at a flow rate not exceeding 250 ml/min as long as it contains at least 30 cm of reduced copper beyond the part already oxidized. The flow rate used was 150 ml/min. It could be controlled by means of a gas washing bottle (6) partly filled with glycerol; the bottle could be attached to the system with a three-way stopcock (A). The tube (3b) is partly filled with sodium sulfate and, above this, with aluminum oxide (according to Brockman for chromatographic analysis). The contents were packed by means of a vibrator and held in position by plugs of cotton. The reaction tubes were attached to the lower part of the tube (3b) with a rubber tube in such a way that the ends of the glass tubes were in close contact. (4) is a cooling trap and (5) a manometer. The whole system can be attached at (A) to a vacuum pump.

The reaction tubes were made from test-tubes with an inner diameter of about 15 mm and a wall thickness of about 0.4 mm. The tubes were constricted in the middle; the open ends were smoothed. The sides of the bulb softened in a flame were pushed in with capillary tubes to increase the surface for better heat transference. At the same time the capillaries promote smooth boiling. The reaction tubes were made to contain about 5 g of monomer.

Parts (3a), (b) and (c) were carefully washed in a solution of sodium dichromate and sulfuric acid and then in water saturated with sulfur dioxide. After rinsing with alcohol and ether tube (3b) was filled with the adsorbents and the pieces (a), (b) and (c) were put together. Where ground joints were not used, the tubes were assembled as closely as possible by means of rubber vacuum tubes covered with picein. When the polymerization was to be performed with an initiator a weighed amount of this was placed in the reaction tube before it was attached. In order to remove the air from the system it was evacuated and filled with nitrogen. When this procedure had been repeated 5—10 times stopcocks (A) and (B) were closed. Monomer was then run into the tube (3c) and slowly sucked through the adsorbents in (3b) into the reaction tube, which was cooled in a mixture of dry ice and alcohol. After the filling was completed the reaction tube was sealed off at the constricted part and a small hook was formed.

Aluminum oxide was used to remove peroxides from the monomer. This method has previously been tried by Dasler and Bauer[13] on ether. They thus obtained an ether which was practically free from all peroxides. Experiments carried out on chloroprene have shown that the amount of peroxides could easily be reduced by about 98 per cent.

Treatment of the polymerizates

In order to calculate the heat of polymerization it is necessary to know the amount of polymer formed during the reaction.

The amount of polychloroprene was determined according to a method by Lewis and Mayo [14]. The polymerization mixture which at high degrees of conversion had a semi-solid consistency, was cut in small pieces and then allowed to swell in benzene. In a freeze drier the benzene and the unpolymerized chloroprene were removed. The polymerizate was slightly heated during the end of the procedure and a constant weight was obtained after about four days.

During the experiments with methyl methacrylate the method of Lewis and Mayo had not come to our attention. The polymerizate was dissolved in chloroform and some hydroquinone was added as a stabilizer. The polymer was then precipitated with methyl alcohol and dried in a vacuum oven at 50° C to constant weight. Evaporation of the supernatant showed that the precipitation was complete. — The polystyrene was treated in the same way.

Other chemical agents

The initiator used was recrystallized benzoyl peroxide (Benzoylperoxid reinst für wissenschaftliche Zwecken, Dr. Theodor Schuckardt, Görlitz, Deutschland).

The heat exchange media in the calorimeter were carbon tetrachloride (analytical grade; boiling point 76.8 ° C and heat of vaporization 46.4 cal/g) for methyl methacrylate and styrene, and chloroform (Baker's analyzed; boiling point 61.5° C and heat of vaporization 59.1 cal/g) for chloroprene.

RESULTS

The results of the measurements are given in Tables 1—3. The heat evolved as a function of time when 1 mole of the monomer polymerizes, is given in Figs. 5 and 7 for methyl methacrylate and chloroprene respectively. The first five experiments in Table 1 were made without any initiator. Experiments 1*, 2* and 4* were run with a monomer from which the peroxides had not been removed. In Fig. 5 the corresponding curves are marked with an asterisk. Evidently the removal of peroxides from the monomer is quite necessary in order to get reproducible results. The mean value of the heat of polymerization obtained in experiments 6—16 is 13.9 $\pm$ 0.3 kcal/monomer unit. From Fig. 6 where the heat of polymerization is plotted as a function of the amount

Table 1. Heats of polymerization of polymethyl methacrylate.

Experiment	Amount of initiator in per cent by weight	Degree of conversion in per cent	Heat of polymerization, $-\Delta H_p$, in kcal/ monomer unit
1*	0	95.7	12.6
2*	0	94.7	13.4
3	0	21.9	12.9
4*	0	94.7	13.2
5	0	68.8	13.4
6	0.017	95.6	13.6
7	0.049	97.9	13.9
8	0.078	77.9	14.1
9	0.084	88.1	14.0
10	0.101	96.1	14.0
11	0.102	96.3	14.0
12	0.50	97.9	14.1
13	0.57	98.0	13.6
14	1.01	93.8	13.4
15	1.03	92.3	14.6
15	1.58	98.5	13.9

Mean value, 6—16: $-\Delta H_p{}^{349.8} = 13.9 \pm 0.3$

Table 2. Heats of polymerization of polystyrene.

Experiment	Amount of initiator in per cent by weight	Degree of conversion in per cent	Heat of polymerization, $-\Delta H_p$, in kcal/ monomer unit
1	1.13	98.8	16.1
2	1.35	97.8	16.2
3	1.89	97.9	16.1

Mean value: $-\Delta H_p{}^{349.8} = 16.1 \pm 0.1$

of initiator, it is evident that no pronounced dependence on the initiator concentration exists. The spread of the values at higher concentrations can be ascribed to a vigorous boiling of the heat exchange medium causing weight losses by splashing. From the three experiments on styrene in Table 2 a mean value of the heat of polymerization of polystyrene of 16.1 ± 0.1 kcal/ monomer unit is obtained. On chloroprene ten experiments were made with various amounts of initiator. From Fig. 8 it is evident that the heat of poly-

Table 3. Heats of polymerization of polychloroprene.

Experiment	Amount of initiator in per cent by weight	Degree of conversion in per cent	Heat of polymerization, $-\Delta H_p$, in kcal/ monomer unit
1	0.08	90.8	15.6
2	0.38	95.4	16.7
3	0.74	98.7	17.1
4	0.88	99.2	17.1
5	1.69	97.7	17.2
6	1.92	100.0	17.3
7	2.19	98.3	17.5
8	2.90	98.5	18.1
9	3.18	98.4	18.1
10	3.43	98.4	18.1

Value extrapolated to zero
concentration of initiator: $-\Delta H_p^{334.5} = 16.2 \pm 0.3$

merization shows a marked dependence on the initiator concentration. The value obtained by extrapolation to zero concentration is 16.2 $\pm$ 0.3 kcal/ monomer unit.
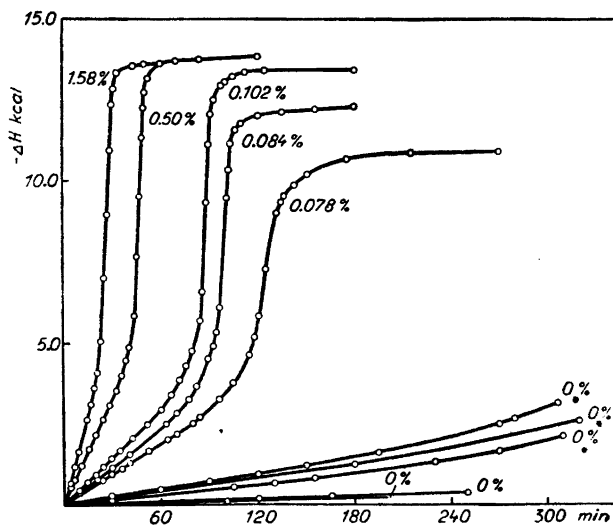

Fig. 5. Heat evolved vs. time when 1 mole of methyl methacrylate is polymerized at different concentrations of initiator.
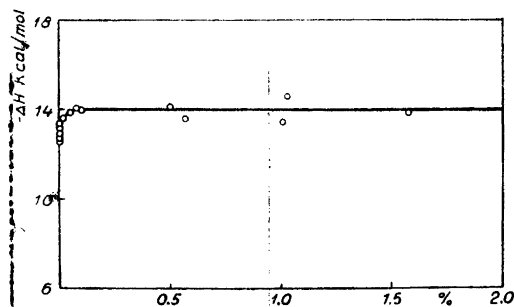
Fig. 6. Heat of polymerization of polymethyl methacrylate vs. amount of initiator.

In calculating the values of the heat of polymerization no corrections have been made for the amount of initiator contained in the macromolecules or for the heat evolved in the activation reaction. These corrections would be large, however, only in a case where a large amount of initiator was used. — Corrections should also be made for the integral heat of dilution. In this case, however, the degrees of conversion are high and judging from heats of swelling given, for instance, by Hock and Schmidt [15] and Gee [16], such a correction is probably less than 1 per cent.
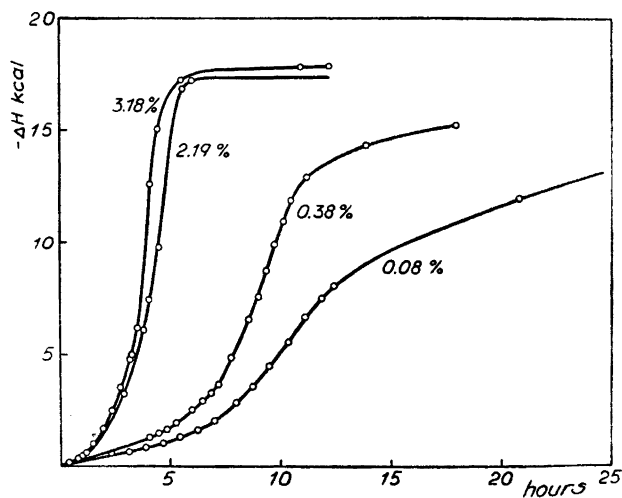

Fig. 7. Heat evolved vs. time when 1 mole of chloroprene is polymerized at different concentrations of initiator.
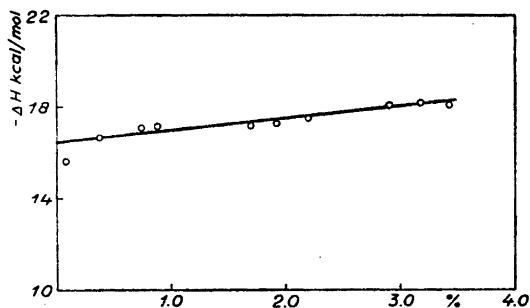
Fig. 8. Heat of polymerization of poly-
chloroprene vs. amount of initiator.

DISCUSSION

As mentioned before the determinations of the heats of polymerization of polymethyl methacrylate and polystyrene were made in order to check the calorimeter. The values determined by other authors are given below:

Polymethyl methacrylate:

$-\Delta H_p$ in kcal/monomer unit	Method		
21.4	Heat of combustion;	ref.	(17)
7.9 ± 0.4	Adiabatic calorimeter;	ref.	(6)
12.9 ± 1.1	Adiabatic calorimeter;	ref.	(7)
13.0 ± 0.2	Isothermal calorimeter;	ref.	(1)
13.0 ± 0.2	Isothermal calorimeter;	ref.	(2)

Polystyrene:

$-\Delta H_p$ in kcal/monomer unit	Method		
10.6	Heat of combustion;	ref.	(18)
14.8	Heat of combustion;	ref.	(18)
21.9	Heat of combustion;	ref.	(19)
23	From the activation energy of polymerization and depolymerization;	ref.	(20)
15.0 ± 0.47	Adiabatic calorimeter;	ref.	(6)
16.68	Heat of combustion;	ref.	(8)
16.1 ± 0.2	Isothermal calorimeter;	ref.	(3)

The value obtained here for polymethyl methacrylate, $-\Delta H_p = 13.9 \pm$ 0.3 kcal/monomer unit, is slightly higher then the values obtained by Tong and Kenyon [1,2] but coincides, within the limits of experimental error, with the value given by Evans and Tyrrall [7]. Tong and Kenyon have not given any values for the degree of conversion. According to our experience this

seldom reaches 100 per cent. The mean degree of conversion from our experiments nos. 6—16 is 93.7 per cent. If a correction for the degree of conversion were applied to Tong and Kenyon's data the value 13.9 ± 0.2 would be obtained. We do not claim that this is the true explanation of the discrepancy. It is very striking, however, that the value obtained here for polystyrene, $-\Delta H_p = 16.1 \pm 0.1$, is in very good agreement with the value obtained by Tong and Kenyon [3]. In our investigation only three determinations have been made; the agreement between them is very good and there is no reason to believe that the values are wrong. — No judgement can be made from our data in Table 2 as to the dependence on the concentration of initiator, which was reported by Tong and Kenyon [3], because of the narrow range of concentrations studied in our experiments.

Some of the polymethyl methacrylates obtained in this investigation have been used by Claesson [21] for adsorption analysis experiments. The frequency curves obtained (Fig. 9) show several maxima as do the curves obtained by means of fractional precipitation on other samples of polymethyl methacrylate (Kinell [22]). The curves in Fig. 9 show that complete reproducibility of the polymerization reaction is difficult to achieve. Comparing curves (e) and (f) corresponding to the amounts of initiator of 0.101 and 0.102 per cent and the degrees of conversion of 96.1 and 96.3 per cent, it is evident that the course of the reaction has not been the same in both cases. Curves (c) and (d) are also different. They correspond to 0.078 and 0.084 per cent of initiator respectively. The discrepancy here is also evident from the curves in Fig. 5. Curves (a) and (b), corresponding to polymers formed from monomers containing only peroxides in the amounts present as impurities, are almost identical in shape; they are only displaced against each other. The experimental material presented does not permit any definite explanation of these discrepancies. It may be pointed out that the rate of the reaction will be so high especially at larger amounts of initiator that the heat evolved can not be conducted away rapidly enough; therefore a rise in temperature will occur and the reaction can not proceed under isothermal conditions. In such a case the size and shape of the reaction tubes play an important role.

The value obtained for the heat of polymerization of polychloroprene, $-\Delta H_p = 16.2 \pm 0.3$ kcal/monomer unit, is in fairly good agreement with the value, $-\Delta H_p = 15.1 \pm 0.8$ kcal/monomer unit, given by Walker [9]. The heat evolved is dependent on the amount of initiator (Fig. 8). The explanation of this can not yet be given. — Flory [23] has made a calculation of the heat of polymerization of different kinds of monomers. For dienes he finds a heat of polymerization of about 20 kcal/monomer unit. In general the experimental values are lower than the calculated ones. An explanation of this has been
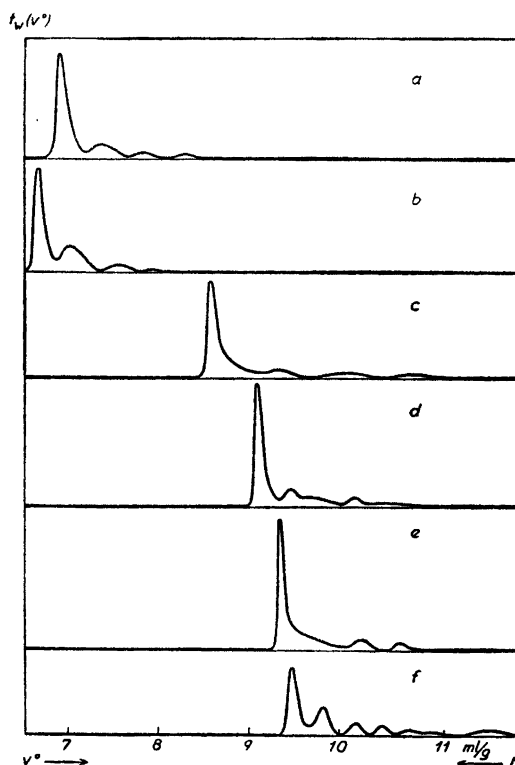
*Fig. 9. Frequency curves of polyme-
thyl methacrylates. v^0 is the specific
retention volume and M the molecular
weight. (From frontal analysis experi-
ments on active carbon by Claesson [21]).*

given by Flory [24] and Evans and Polanyi [25]. During polymerization the mono-
mer units can arrange themselves in various ways. It is possible to get both
"head-to-tail" and "head-to-head, tail-to-tail" arrangements. In some cases
it has been possible to determine the actual arrangement. Thus polyisobutylen
has a head-to-tail structure (Thomas *et al.* [26] and Fuller, Frosch and Pape [27]).
In these molecules, however, there are very large steric hindrances which are
responsible for the observed low heat of polymerization. In the case of poly-
chloroprene roentgenographic measurements (Kenney [28], Garbsch and von
Susich [29], Fuller [30], Birkett Clews [31] and Lindgren [32]) have shown that on
stretching to 200—300 per cent elongation some of the molecules orient them-
selves to a crystalline structure which has a fibre period of 4.79 A. This value
is in agreement with a *trans*-configuration of the crystallized polychloroprene
(*cf.* Mark [33]). In a chain with this configuration built up from Fisher-Stuarts
molecular models no steric hindrances can be located. A *cis*-configuration,
however, seems to show such hindrances. On stretching only a comparatively
small amount of the polymer will be oriented; therefore the possibility is not

excluded that a *cis*-configuration can predominate in the amorphous parts of the polymer. Furthermore some of the macromolecules may have been formed by 1,2-addition which gives a very compact structure compared to the 1,4-addition. All these facts make it probable that the heat of polymerization of polychloroprene has a value lower than about 20 kcal/monomer unit.

SUMMARY

An isothermal calorimeter for determination of heats of polymerization has been described. Measurements made on polymethyl methacrylate, polystyrene and polychloroprene formed by initiation with benzoyl peroxide from monomers which have been purified from peroxides by means of aluminum oxide, have given the following heats of polymerization:

Polymethyl methacrylate $- \Delta H_p^{349.8} = 13.9 \pm 0.3$ kcal/monomer unit

Polystyrene $- \Delta H_p^{349.8} = 16.1 \pm 0.1$ »   »   »

Polychloroprene $- \Delta H_p^{334.5} = 16.2 \pm 0.3$ »   »   »

The heat of polymerization of polychloroprene shows a dependence on the amount of initiator. The reason for this can not yet be given.

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