ACTA CHEMICA SCANDINAVICA 3 (1949) 1—12

On the Change in Particle Size Distribution of Polymethyl Methacrylate during Polymerization

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In an investigation of some commercial samples of polymethyl methacrylate Kinell[1] has shown that the mass-frequency curves of these substances had at least three maxima. The samples had probably been prepared in bulk polymerization. Therefore it has been regarded of interest to study this type of polymerization especially with respect to the distribution of particle sizes and the change in this distribution during polymerization. The preliminary results of these measurements are presented in this paper.

The polymerization of vinyl compounds takes place in at least three steps. The first of these is the activation of the monomer. This can be done thermally, photo-chemically or by means of a suitable initiator. The monomeric molecule will in all these cases be transfered into an excited state. In this investigation benzoyl peroxide has been used as an initiator. It can be assumed that the benzoyl peroxide is split into two radicals according to one of the following two formulae:

$$(C_6H_5CO_2)_2 \rightarrow 2\ C_6H_5CO_2^* \qquad (1)$$

$$(C_6H_5CO_2)_2 \rightarrow 2\ C_6H_5^* + 2\ CO_2 \qquad (2)$$

These radicals react with the monomer to a new radical. In this way the reaction chain leading to the formation of polymeric molecules is started. Denoting the initiator molecule with R_2, the radicals formed in the dissociation of the initiator with R^* and the monomer with M, we get the following reaction scheme:

$$R_2 \longrightarrow 2R^* \qquad (3)$$

$$R^* + M \longrightarrow M^* \qquad (4)$$

$$M^* + M \longrightarrow M_2^*$$

$$M_n^* + M \longrightarrow M_{n+1}^* \qquad (5)$$

The reaction should proceed indefinitely if the growing molecule could not in different ways undergo deactivation. Firstly this can occur if a hydrogen atom is transfered from either a monomer molecule, a polymer molecule, M_n, or a molecule from the solvent, T, etc. In this case a new radical will be formed. Secondly two growing molecules can react and form one stable molecule. Thirdly a transfer of a hydrogen atom can occur between two growing molecules. In this case two stable polymer molecules will be formed, one of which contains a carbon-carbon double bound. These posibilities are summerized in the following formulae:

$$M_n^* + M \longrightarrow M_n + M^* \tag{6}$$

$$M_n^* + M_m \longrightarrow M_n + M_m^* \tag{7}$$

$$M_n^* + T \longrightarrow M_n + T^* \tag{8}$$

$$M_n^* + M_m^* \longrightarrow M_{n+m} \tag{9}$$

$$M_n^* + M_m^* \longrightarrow M_n + M_m \tag{10}$$

Evidence that the initiator is split into free radicals according to reaction (3) can be obtained if the polymer is analyzed for these radicals. Each polymer molecule must contain at least one such radical if the assumption is correct. Measurements of this kind have been made on polystyrene [2] and on polymethyl methacrylate [3]. As regards reaction (8), this transfer of hydrogen atoms can be performed by means of intentionally added substances — chain transfer substances. This is often done in order to affect the mechanical properties of the polymer. The chain transfer reaction does not change the amount of free radicals and hence the overall rate of reaction is not affected, presupposing that the reactivity of the new radical is the same as that for a growing molecule. The molecular weight of the polymer will, however, be lower.

In the bulk polymerization of methyl methacrylate the rate of reaction increases very slowly in the beginning. At 10—20 per cent conversion the rate increases very rapidly and all the remaining monomer can be polymerized in a few minutes. The reaction is almost »explosive». Finally the reaction ceases because the monomer is used up. Due to the amount of heat liberated during the polymerization (for polymethyl methacrylate Tong and Kenyon [4] have determined the heat of polymerization to 13.0 ± 0.2 kcal/mol) a considerable rise in temperature can be expected within the reaction mixture during the explosive part of the reaction. An increase in temperature of about 100° C has been observed by Norrish and Brookman [5] and Schulz and Blaschke [6] for bulk polymerization of methyl methacrylate. In kinetic measurements it is therefore of importance to find out the extent to which it is possible to maintain an isothermal state. No reliable results can be obtained unless this condition can be fulfilled.

It is of interest in this connection to give a short discussion of the reasons for the explosive course of the polymerization reaction. The following three possibilities can be quoted.

Firstly the polymer is a very bad heat conductor. Thus the liberated heat of polymerization has to be removed by means of convection currents in the reaction mixture. This will be the more difficult the higher the degree of conversion, because the viscosity of the mixture increases rapidly. As a consequence of this the temperature rises as does the rate of reaction.

Secondly, Schulz and Blaschke[7] have assumed that each growing molecule can in some way give rise to the formation of two or even more activated molecules. Thus the total amount of activated molecules is increased and the rate of reaction will be higher.

Thirdly, according to Norrish and Smith[8], the deactivation of the growing molecules will be rendered more difficult the higher the viscosity of the mixture. The amount of free radicals is increased and thus the rate of reaction is becoming higher.

The first of these possibilities is of course quite true. However, Norrish and Smith[8] have shown that the explosive course of the reaction does occur even at lower temperatures. In an experiment with methyl methacrylate at a temperature of 25° C they were able to keep the reaction temperature constant within a tenth of a degree, and yet the conversion versus time curve had the same shape as at higher temperatures. Thus the influence of temperature on the reaction rate is of second hand importance. According to the theory of Schulz and Blaschke their conclusion depends upon the result that the degree of polymerization does not change with time. This result is, however, in agreement neither with measurements of Norrish and Brookman nor with the results which will be reported in this paper. Later Schulz and Harborth[9] have published an investigation in which the results of Schulz and Blaschke concerning the constant degree of polymerization are explained as being due to the fact that the polymerisations were not performed isothermally.

The theory of Norrish and Smith is founded on the following observations. According to Norrish and Brookman the mean molecular weight increases approximately in proportion to the amount of polymer formed. Furthermore the increase in rate of reaction occurs at a higher degree of conversion if the polymerization is performed at a higher temperature or with a larger amount of initiator. In both these cases a polymer with a lower molecular weight is formed and hence the viscosity of the reaction mixture is lower. Another piece of evidence for this theory has been given by Eriksson (unpublished). The dimensions of the reaction ampoules have been shown to have no influence on the reaction rate. This is true for ampoules with not too large dimensions. Thus the warming up of the reaction mixture is not of primary importance. The present investigation also will give some contributions to this question.

EXPERIMENTAL

The method used in the polymerization experiments was essentially the same as that used by Norrish and Brookman[5]. The reaction was performed at 80 °C and in small, evacuated tubes of glass containing 4—5 ml monomer, immersed in a thermostat. In order to be able to follow the change in conversion with time, about ten tubes were used for each amount of initiator. After given time intervals the tubes were taken up and cooled down in melting ice to zero degrees. The time elapsing between the moment when the tube was immersed in the thermostat and cooled down in the ice bath was used as the time of polymerization. The amount of polymer formed was determined by dissolving the reaction mixture in acetone. This solution was poured with stirring into methanol. The precipitated polymer was dried to constant weight in vacuum at room temperature. The different polymers were characterized by determining their intrinsic viscosity in an Ostwald viscosimeter.

The monomer was distilled four times at ordinary pressure. Each time about 10—15 per cent of the monomer was allowed to polymerize in the distillation bulb. This was done intentionally in order to remove from the monomer all inhibiting or foreign chain transfering substances, which could possibly have an influence upon the molecular weight of the polymer formed. As is seen in the following this monomer has a rather great tendency to polymerize without any initiator. Therefore one must not exclude the fact that it contains small amounts of peroxides formed with atmospheric oxygen.

The initiator used was recrystallized benzoyl peroxide marked »Benzoylsuperoxid reinst, für wissenschaftl. Zwecken. Dr. Theodor Schuchardt, Görlitz, Germany».

RESULTS

The results obtained in five polymerization experiments with different concentrations of initiator are summarized in Table 1. At a conversion of 15—20 per cent the reaction rate starts to increase rapidly. The intrinsic viscosity increases simultaneously to about twice its earlier value. Further information about the course of the polymerization can be obtained by using Schulz's[10] statement that the intrinsic viscosity of polymethyl methacrylate is proportional to the number average of the molecular weight. Dividing the amount (m) of polymer formed with the intrinsic viscosity $[\eta]$ a number is obtained which is proportional to the number of polymer molecules formed. In this way the curves in Fig. 1 have been constructed. The number of mole-

Table 1. Degree of conversion and intrinsic viscosity as a function of time in polymerization of methyl methacrylate in bulk with different amount of initiator. Temperature of reaction: 80° C. Initiator: benzoyl peroxide. Intrinsic viscosity measured in chloroform solution and calculated with 1 g polymer in 100 ml solution as a concentration unit; all values extrapolated to zero concentration.

Concentration of initiator zero		
Time of reaction in min	Degree of conversion in per cent	Intrinsic viscosity
73	4.1	—
167	11.5	4.50
313	23.8	7.18
Concentration of initiator 0.99 · 10^{-6} g mol per ml		
30	5.7	3.14
60	11.1	3.29
75	14.4	—
85	16.8	3.58
100	20.2	—
115	26.0	4.00
130	30.4	—
145	43.1	4.80
160	77.7	6.52
200	91.7	6.95
Concentration of initiator 20.6 · 10^{-6} g mol per ml		
11.5	8.8	1.02
20	16.9	1.10
31	26.2	1.16
96	96.3	2.20

Concentration of initiator 2.01 · 10^{-6} g mol per ml		
Time of reaction in min	Degree of conversion in per cent	Intrinsic viscosity
30	7.7	2.68
64	16.4	2.87
75	19.6	—
94	27.2	3.12
115	52.0	4.48
126	85.0	6.30
132	89.4	—
152	92.3	—
180	91.8	—
210	93.3	—
240	93.0	—
287	93.4	6.55
Concentration of initiator 41.3 · 10^{-6} g mol per ml		
10	10.5	0.75
15	17.5	0.82
30	40.1	1.08
90	96.2	1.43

cules formed is a linear function of time at all concentrations of initiator used. The linearity ceases as soon as the reaction starts to be explosive. In this part of the reaction the number of molecules formed per unit of time increases until most of the monomer is used up.

The dependence of the reaction rate on the amount of initiator can be seen from Fig. 2, where the quantity $m/[\eta] \cdot t$ for the first part of the reaction has

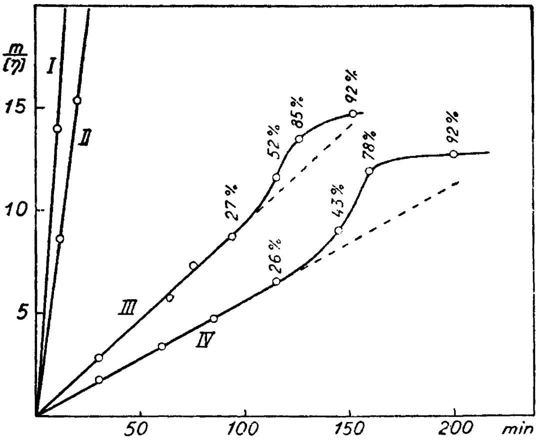

Fig. 1. Number of molecules formed as a function of time at different concentrations of initiator, I: 41.3 · 10^{-6} g mol/ml, II: 20,6 · 10^{6} g mol/ml, III: 2.01 · 10^{-6} g mol/ml, IV: 0.99 · 10^{-6} g mol/ml. The numbers on curves III and IV represent the corresponding degrees of conversion.

been plotted against the original amount of initiator. The points do not correspond to a straight line. This can be understood by assuming that a chain transfer occurs between growing polymer and monomer (reaction (6)). For a stationary condition, *e. g.* activated molecules are formed at the same rate in reaction (3) as they are consumed in reactions (9) or (10) the following expression is obtained:

$$[\mathrm{M}^*] = \mathrm{const.}\sqrt{[\mathrm{R}_2]} \tag{12}$$

where $[\mathrm{M}^*]$ and $[\mathrm{R}_2]$ are the concentrations of activated molecules and initiator molecules respectively. The rate of reaction is determined from:

$$\frac{\mathrm{d}\,[\mathrm{N}]}{\mathrm{d}t} = k_6\;[\mathrm{M}]\;[\mathrm{M}^*] + k_9\;[\mathrm{M}^*]^2 + k_{10}\;[\mathrm{M}^*]^2 \tag{13}$$

if a cessation reaction of type (7) is disregarded in this early stage of the polymerization. [N] is the concentration of polymer molecules. Using equ. (12) one obtains:

$$\frac{\mathrm{d}\,[\mathrm{N}]}{\mathrm{d}t} = a \cdot \sqrt{[\mathrm{R}_2]} + b\;[\mathrm{R}_2] \tag{14}$$

The curve drawn in Fig. 2 corresponds to an expression of this type, namely:

$$\frac{m}{[\eta] \cdot t} = 26.5\,\sqrt{C} + 30.3 \cdot 10^3\,C \tag{15}$$

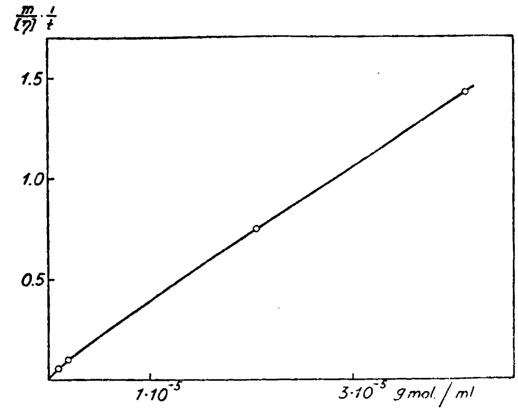

Fig. 2. Rate of reaction as a function of amount of initiator.

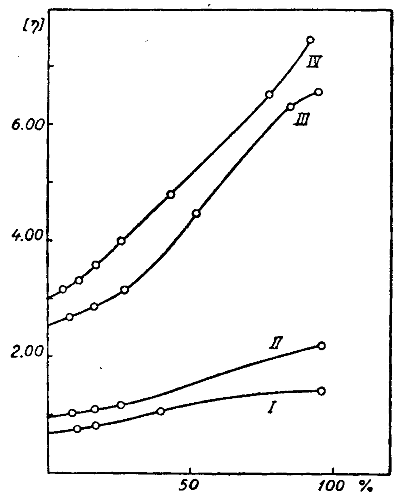

Fig. 3. Intrinsic viscosity as a function of degree of conversion. For further explanation cf. Fig. 1.

where C is the original concentration of the initiator. This shows that a chain transfer reaction of type (6) exists. In some investigations to determine the rate constants of the chain reaction Bamford and Dewar[11] have shown that such a chain transfer reaction is important in the thermal polymerization of styrene. During the later part of the polymerization reactions of the type (9) and (10) are suppressed due to the increasing viscosity of the reaction mixture. Thus the mean life of the activated molecules is longer and their chance to deactivate according to reaction (6) is greater. Each reaction chain will be comprised of a larger number of molecules. This gives a higher value of $d\,[N]/dt$. At a conversion of about 75 per cent the lack of monomer causes both the rate of polymerization and the rate of formation of polymer molecules to decrease. The polymerization ceases completely at a conversion of 92—96 per cent depending upon whether the amount of initiator is low or high.

It can be expected that the influence of the changes in the reaction mixture on the process of deactivation will cause the polymer formed to be very inhomogeneous. In order to obtain qualitative information about this, a study has been made of the relation between intrinsic viscosity $[\eta]$, and degree of conversion, m. According to the results in Fig. 3 the intrinsic viscosity increases with the degree of conversion for all amounts of initiator used. The intrinsic viscosities, however, are mean values for all the polymer molecules

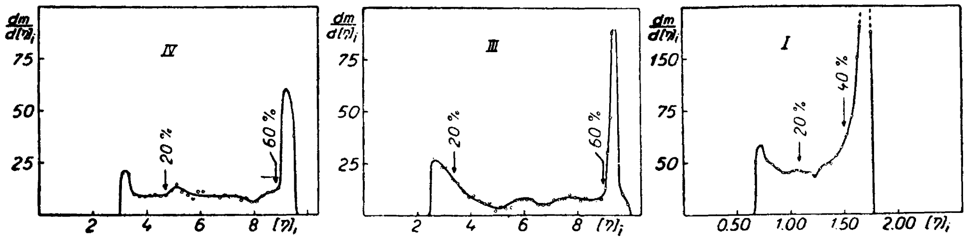

Fig. 4. Mass-frequency curves of polymethyl methacrylate formed at a concentration of initiator of $0.99 \cdot 10^{-6}$ *(IV),* $2.01 \cdot 10^{-6}$ *(III) and* $41.3 \cdot 10^{-6}$ *(I) mol/ml respectively.*

formed during a certain time interval. A more suitable quantity for this discussion is the increment in intrinsic viscosity, $[\eta]_i$. This is defined as the mean viscosity of all the polymer molecules formed at a certain degree of conversion. Wall[12] has indicated a simple way to calculate this quantity from the relation between $[\eta]$ and m. If a polymer molecule is formed very rapidly, it can be referred to a definite degree of conversion. Assuming that this molecule cannot later take part in the reaction for instance through reaction (7), one obtains:

$$[\eta] = \frac{\int_0^m [\eta]_i \mathrm{d}m}{\int_0^m \mathrm{d}m}$$

and after differentiation:

$$[\eta]_i = [\eta] + \frac{\mathrm{d}[\eta]}{\mathrm{d}m} \cdot m$$

The derivative $\mathrm{d}[\eta]/\mathrm{d}m$ can be calculated graphically from Fig. 3. Plotting m against the obtained values of $[\eta]_i$ the mass-distribution curves of each polymer are obtained. The derivatives of these curves give the mass-frequency curves of the polymer in question. These curves are shown in Fig. 4. The arrows demarcate the parts which are formed during the stationary, the explosive and the final stage respectively. The per cent numbers give the degrees of conversion. These curves are of course rather inaccuarate as the experimental errors are quite large. This is especially true for curve I. Furthermore, it must be pointed out that they are not true frequency curves, as the viscosity increment is a mean value too. Some conclusions can, however, be drawn. All curves have the same general shape. The peak to the left is probably the beginning of a normal frequency curve, *e. g.* a curve which should be obtained if the polymerization could proceed during the entire time according to the conditions which prevail during the first stage. Such a curve can be

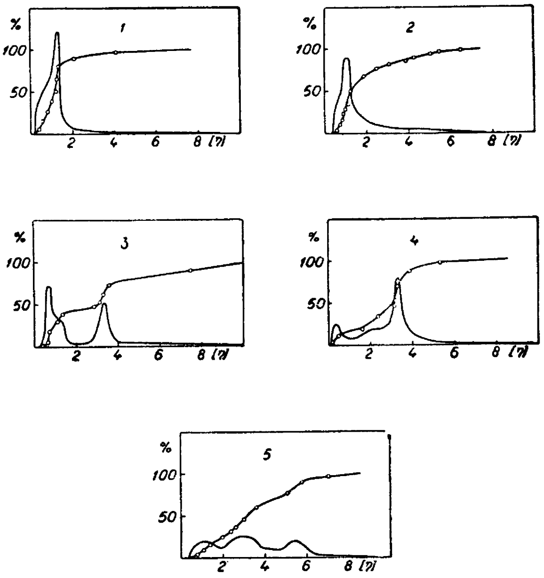

Fig. 5. Mass-distribution and mass-frequency curves of samples of polymethyl methacrylate taken at degrees of conversion of 11.2 (1), 28.4 (2), 53.2 (3), 83.2 (4), and 93.6 (5) per cent respectively.

calculated from the reaction scheme and has only one maximum. In this case, however, the explosive stage of the reaction complicates the frequency curves. The cessation reactions cannot proceed in a normal way and the molecules are getting larger. The large peak to the right can be explained, if a chain transfer reaction of type (6) predominates. This will put an upper limit on the growth of the activated molecules.

In order to get more reliable information about the change in particle size distribution during the polymerization, five samples of polymethyl methacrylates were prepared. All of them were made from the same monomer at a constant temperature of 80° C and with benzoyl peroxide as an initiator in a concentration of $5.49 \cdot 10^{-6}$mol/ml. The time of polymerization was choosen in such a way that samples corresponding to suitable degrees of conversion were obtained: 11.2, 28.4, 53.2, 83.2, and 93.6 per cent respectively. The samples were divided up into a number of fractions by means of fractional precipitation with cyclohexane from benzene solutions. The intrinsic viscosities of the fractions were measured in benzene solution and the mass-distribution curves constructed according to Schulz. From these, the mass-frequency curves were calculated. All the curves are shown in Fig. 5. Samples 1 and 2 have frequency curves with only one maximum at $[\eta] = 1.3$ and 1.1 respectively. Both of the curves are skew. Sample 2 contains more high molecular material than sample 1. At higher degrees of conversion, frequency curves with two maxima are obtained (samples 3 and 4). The maximum to the right is in both cases situated at $[\eta] = 3.3$. The maximum to the left corresponds to a rather high amount of substance with a rather low molecular weight (sample 3). For high degrees of conversion this maximum seems to be divided up in two maxima (sample 4). At still higher conversions all the maxima seem to flatten out (sample 5). The last frequency curve shows striking similarities with the curves in Fig. 4. This curve is, however, different from the curves obtained by Kinell but as the degree of conversion for his samples were not known, a comparison can hardly be made. The general shape of the curves is the same.

No profound discussion of these curves can be given at this early stage of the present investigation. Some remarks will, however, be made as to the skewness of the frequency curves of samples 1 and 2. One may suppose that the skewness depends upon a competition between various reactions. Assuming a stationary state the discussion can be limited to reactions (5), (6), (9), and (10) if only the first period of the polymerization is taken into account. Denote by p_1, the probability that a growing molecule will add another monomer (reaction (5)), by p_2 the probability that the same molecule will undergo chain transfer (reaction (6)), by p_3 the probability that it will react with another growing molecule giving two deactivated molecules (reaction (10)) and finally by p_4 the probability, that it will react with another growing molecule giving only one deactivated molecule (reaction (9)). All these probabilities are independent of the degree of polymerization presupposing that the reactivity of the growing molecules is always the same. If the final fate of the growing molecule is limited only to one or more of these reactions we have:

$$p_1 + p_2 + p_3 + p_4 = 1$$

The probability that a growing molecule will form a polymer molecule with the degree of polymerization n is $p_1^{n-1}p_2$, $p_1^{n-1}p_3$ or $^1/_2\, p_1^{n-2}p_4\, (1-p_1)\, (n-1)$ for the cessation reactions (6), (10) or (9) respectively. The massfrequency curve is then given by the expression:

$$\mathrm{f}(n) = \frac{(1-p_1)^2}{2(p_2+p_3)+p_4}\left[2(p_2+p_3)\,p_1^{n-1}n + p_4\,(1-p_1)\;p_1^{n-2}\,(n-1)n\right] \qquad (16)$$

with

$$\sum_1^{\infty} \mathrm{f}(n) = 1$$

This function, however, cannot have inflexion points in the same way as the frequency curves of samples 1 and 2. It is also difficult to find values on the probabilities p_1, p_2, p_3, and p_4, which give the very rapid decrease in the experimental frequency curves at increasing molecular sizes. The discrepancies between the experimental and theoretical curves are probably due to changes in reactivity of the growing molecule with the degree of polymerization. With increasing weight the thermal motion of the molecules will be slower and hence the number of collisions between molecules will diminish. Furthermore a long, growing molecule may screen off its own reactive center. In both of these cases the possibility of further reaction is reduced.

The previous discussions can be summarized in the following conclusion. It is convenient to divide the polymerization reaction into three phases. During the first phase, the stationary stage, the polymerization and initiation rates are both constant. Deactivation of growing radicals occurs during this period both by chain transfer and by a bimolecular reaction between two growing chains. During the second phase, beginning at a conversion of 10—20 %, the reaction mixture is so viscous that the deactivation between growing radicals ceases to occur or at least is rendered more or less difficult. As a consequency during this stage of polymerization radicals are obtained with a longer average lifetime. Thus the same kinetic chain can give rise to a larger number of stable molecules than during the first stage. The rate of polymerization increases and the molecular weight of the polymer will be higher. The third phase is characterized by the gradual cessation of the reaction. The chain transfer here imposes an upper limit on the growth of the polymer radicals. The polymerization stopes entirely at a conversion of 92—96 % depending upon whether the initial concentration of initiator is low or high. The three maxima of the mass frequency curve of the final product seem to correspond to the three different stages of the polymerization.

SUMMARY

The change in degree of conversion and intrinsic viscosity with time have been studied for the polymerization of methyl methacrylate in bulk using benzoyl peroxide as an initiator. Distribution and frequency curves have been obtained both at various amounts of initiator and at various degrees of conversion. These curves show several maxima. The influence of different types of cessation reactions on the distribution of molecular sizes have been discussed.

This investigation is a part of some research work carried out at the request of AB. Bofors Nobelkrut, Bofors, and the Government Commission on Industry in Sweden.

The author wishes to acknowledge his indebtness to Professor The Svedberg for his very kind interest and for the many facilities which have been put at the author's disposal.

The author also wishes to thank Fil.lic. P.-O. Kinell for his interest in this work and for many valuable discussions.

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Received November 12, 1948.