578. *The Polymerisation of Methacrylamide and the Alkaline Hydrolysis of the Polymer.*

By C. L. Arcus.

The preparation of methacrylamide and its polymerisation in toluene and in ethyl acetate, catalysed by benzoyl peroxide, are described. The polymer is soluble in water and hygroscopic.

Rates of alkaline hydrolysis of acetamide, methacrylamide, and polymethacrylamide at 97° have been determined. The first two amides are rapidly and completely hydrolysed; the hydrolysis of polymethacrylamide proceeds fairly rapidly until 70% of the original nitrogen content has been evolved as ammonia and then becomes very slow. An explanation of the incomplete hydrolysis is put forward in which the steric and polar effects of hydrogen bonding between the remaining amide groups and adjacent carboxyl ions inhibit further reaction with hydroxyl ions.

Groups attached to a large (polymeric) molecule are modified in reactivity by steric and polar factors characteristic of the molecule. The present work is part of an attempt to elucidate the effects of these factors. It is desirable to select for investigation reactions which can be carried out with reagent and polymer in homogeneous solution. Polymethacrylamide, which is soluble in water, has been prepared, and its alkaline hydrolysis studied.

Bruylants and Castille (*Bull. Sci. Acad. roy. Belg.*, 1927, **13**, 779) prepared a somewhat impure specimen of methacrylamide and found that on boiling its solution in benzene an amorphous polymer was formed. The preparation of the monomer from acetone cyanohydrin is described in U.S.P. 2,140,469, and the preparation of aqueous solutions of the interpolymers of methacrylamide with methacrylic and maleic acids, with potassium persulphate as catalyst, is described in B.P. 475,671. No satisfactory description of the preparation of polymethacrylamide has been found.

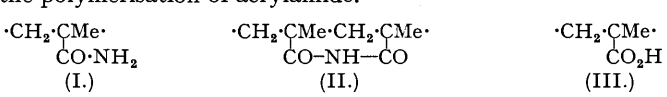
Methacrylamide, $CH_2{:}CMe{\cdot}CO{\cdot}NH_2$, was prepared by shaking methyl methacrylate with excess of ammonia at room temperature for 7 days. Polymerisation, catalysed by benzoyl peroxide, was effected in solution in toluene. It was found that the following conditions are necessary in order to obtain a satisfactory yield of polymethacrylamide: (*a*) a concentrated solution of monomer, obtained by using toluene at its b. p., 111°, which lies at the m. p. of methacrylamide, 110—111° (it is necessary to avoid so great a concentration that when partial polymerisation has occurred an almost solid mass is formed); (*b*) addition of the benzoyl peroxide (2·4% of the weight of the monomer) in small quantities over a period and not as a single addition; (*c*) maintenance of an atmosphere of nitrogen. The total reaction time was 3·5 hours.

Experiments, otherwise identical, having 4 : 1, 3 : 1, and 2·5 : 1 (ml. : g.) ratios of toluene to methacrylamide gave respectively 75, 78, and 89% yields of polymethacrylamide. The intrinsic viscosities of 1% aqueous solutions of these polymers, *viz.*, $[\eta]_c = (1/c) \ln \eta_{soln.}/\eta_{H_2O}$, where c = g. of polymer in 100 ml. of solution, were respectively 0·55, 0·61, and 0·12.

The most concentrated polymerisation solution gave the highest yield of polymer but with a marked reduction in average molecular weight. Polymerisation was also carried out in solution in ethyl acetate, in which the maximum attainable concentration is lower than in toluene and the maximum temperature is limited by the b. p. (77°); reaction for 20 hours with 5·0% of benzoyl peroxide gave a 45% yield of polymethacrylamide having $[\eta]_c$ 0·09.

Polymethacrylamide was obtained as a fine, white hygroscopic powder; the dry polymer when kept at 80% relative humidity for 24 hours absorbed 24% of its weight of water.

The monomer contained the theoretical quantity of nitrogen, 16·5%. Two specimens of polymethacrylamide (A and B, see Experimental) contained respectively 14·8 and 14·9% of nitrogen. The lowering of the nitrogen content below that for $[\cdot CH_2{\cdot}CMe(CO{\cdot}NH_2)\cdot]_n$ is caused by the presence of phenyl and benzoate end-groups from the benzoyl peroxide, and to some hydrolysis and imide formation occurring during the removal of solvent from the polymer, which was effected by alternate heating and maintenance in a vacuum. Similar but more extensive imide formation was observed by Staudinger and Urech (*Helv. Chim. Acta*, 1929, **12**, 1107) during the polymerisation of acrylamide.



(I.) (II.) (III.)

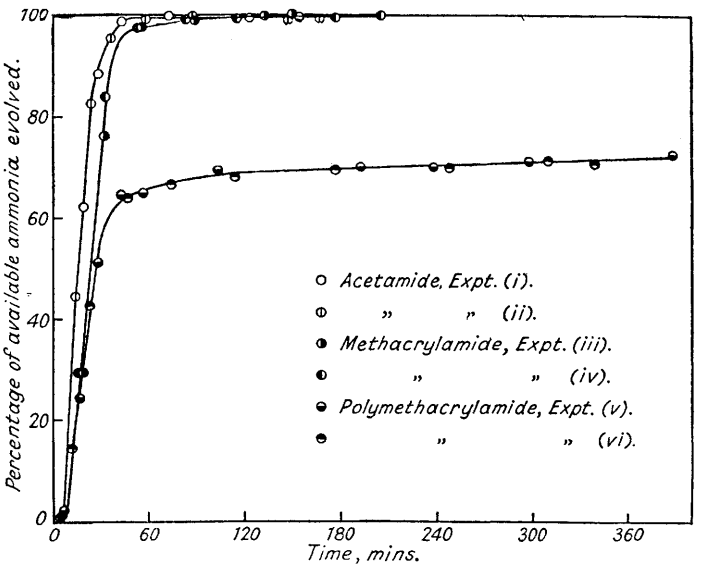
The percentage weights (*i.e.*, g. of unit in 100 g. of polymer) of amide units (I) (N, 16·5%), imide units (II) (N, 9·1%), acid units (III), and end groups (Ph and $Ph{\cdot}CO_2$) in the polymer

(preparation B) have been estimated in the following way. The content of end groups is considered (from data described below) to be 2·3%. The acid-unit content was found, by titration of the polymer, to be 4·6%. The percentage weights, x and y, of amide and imide units can be found from the equations

$14{\cdot}9 = (16{\cdot}5x + 9{\cdot}1y)/100$ and $x + y + 2{\cdot}3 + 4{\cdot}6 = 100$ whence $x = 87{\cdot}2$ and $y = 5{\cdot}9\%$.

Part of this specimen was subjected to hydrolysis in 3·7N-sodium hydroxide for 2 hours, and on acidification the hydrolysed polymer (75% of the original weight) was precipitated. It contained N, 4·9%; the incompleteness of hydrolysis is discussed below. In order to permit calculation, the assumption has been made that during hydrolysis all the imide rings are opened, yielding amide and carboxyl groups (of which the former may further hydrolyse to carboxyl). With this assumption, the nitrogen content, 4·9%, is equivalent to 29·9% of amide units. The content of acid units was found by titration to be 67·8%. The content of phenyl and benzoate end groups, is, by difference, 2·3%. This value has been applied, above, to the original polymer.

FIG. 1.



When attempts were made to estimate the amide content of polymethacrylamide by alkaline hydrolysis and titration of the ammonia evolved, it was found that the reaction does not go to completion. Further, as already described, the polymer isolated from the alkaline hydrolysis of polymethacrylamide had a nitrogen content 33% of that of the original polymer.

The rates of hydrolysis of acetamide, methacrylamide, and polymethacrylamide (preparation B) in 1·8N-sodium hydroxide at 97° have been determined (see Fig. 1). The progress of reaction was followed by periodical estimation of the evolved ammonia as described on p. 2735. Acetamide and methacrylamide were rapidly and completely hydrolysed; hydrolysis of polymethacrylamide proceeded until 70% of the total nitrogen content had been evolved and then became very slow. The percentage of available nitrogen evolved has been calculated for acetamide and methacrylamide from the theoretical nitrogen contents, and for polymethacrylamide from the experimental value, 14·9%.

The following second-order constants (in moles^{-1} ml. min.$^{-1}$) have been calculated from the data of Fig. 1.

Amide.	Period, mins.	k.	Amide.	Period, mins.	k.
Acetamide	14—36	76	Polymethacrylamide	12—23	21
Methacrylamide	16—56	57	,, ...	23—47	12
			,, ...	47—114	1·6

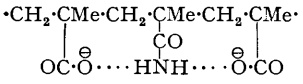
$$k = 2{\cdot}303v[(\log (b - x) - \log (a - x) - (\log b - \log a)]/t(b - a).$$

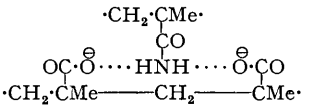
where a, b, and x are moles, respectively, of amide, sodium hydroxide, and ammonia evolved, v is the volume (in ml.), and t the time (in mins.).

When 70% of the nitrogen content of polymethacrylamide had been evolved, there remained N, 4·5%, equivalent to 27·2% of amide units. Of the groups present in the original polymer, the imide units, 5·9%, yielded on hydrolysis 3·3% of acid units and 3·3% of amide units; the latter together with the 87·2% of amide units originally present total 90·5%, of which 27·2% remained unhydrolysed, whence 63·3% were hydrolysed, yielding 64·1% of acid units. There were 4·6% acid units in the original polymer, and the hydrolysed polymer therefore contained 3·3 + 64·1 + 4·6 = 72·0% of acid units. (These percentage weights relate to the weight of the original polymethacrylamide.) The ratio of amide groups to carboxyl groups at this point was 27·2/85·1 : 72·0/86·1 or 1 : 2·6.

The cessation of hydrolysis is attributed to the effects of hydrogen bonding of the amide groups by carboxyl ions. One amide group can undergo bonding with one or with two carboxyl ions, and the latter may be adjacent to the amide group (IV) or attached to another part of the chain or to a different molecule (V). Through the formation of structures of types (IV) and (V) hydrogen bonding causes the polymer molecules to take up more compact

(IV.)

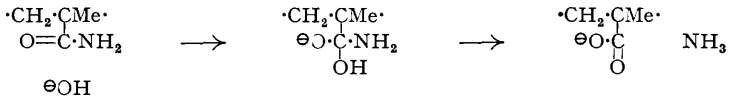




(V.)

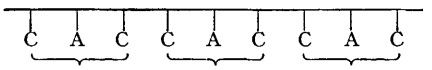
arrangements and the approach of hydroxyl ions is hindered. The effectiveness of the steric hindrance is increased by the methyl groups attached to the carbon atoms which are α- to the amide and carboxyl groups.

Further, a polar effect arises from the hydrogen bonding. The N–H electron-pair is partly released towards the nitrogen atom and a fractional negative charge is relayed to the amide carbon atom. The approach of the hydroxyl ion in the first stage of hydrolysis

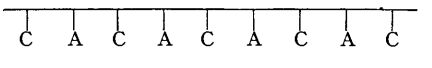


is rendered more difficult by this polar effect. The experimental results described above indicate that when the ratio of carboxyl ions to amide groups attains the value 2·6 : 1 the combined steric and polar retardation effects reduce the rate of hydrolysis nearly to zero.

It is possible that the polymer, when this state has been reached, has a structure in which each amide group is bordered by two carboxyl ions which form hydrogen bonds only with the given amide group; *i.e.*, structures of type (VI) are present but not those of type (VII).

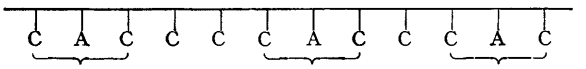


(VI.)



(VII.)

The minimum carboxyl : amide ratio necessary to fulfil these conditions is 2 : 1, and for this the arrangement of groups shown in (VI) is required. The random hydrolysis of amide groups in polymethacrylamide is unlikely to lead to the optimum distribution (VI) of carboxyl ions;



(VIII.)

at the cessation of hydrolysis when the conditions of hydrogen bonding described above are present, the carboxyl : amide ratio exeeds 2 : 1 and the structure of the polymer is of type (VIII).

Experimental.

Methylene chloride was washed with potassium carbonate solution, dried (K_2CO_3), distilled, and the fraction of b. p. 41—41·5° collected. Ethyl acetate was washed twice with sodium carbonate solution, twice with water, dried ($CaCl_2$), distilled, and the fraction of b. p. 76·5—77·5° collected. Toluene was washed thrice with dilute hydrochloric acid, thrice with 3N-sodium hydroxide, dried (K_2CO_3), distilled, and the fraction of b. p. 110·5—112° collected. Methyl methacrylate was washed thrice with N-sodium hydroxide, thrice with water, dried ($CaCl_2$), distilled, and the fraction of b. p. 100—101·5° collected.

Benzoyl peroxide was dried ($CaCl_2$) in a vacuum; the peroxide content, determined by reaction with sodium iodide in acetic anhydride solution and titration of the liberated iodine with sodium thiosulphate (Nozaki, *Ind. Eng. Chem. Anal.*, 1946, **18**, 583), was (i) 97·8, (ii) 98·3%.

Methacrylamide Monomer.—Methyl methacrylate (76 g.) was shaken mechanically with ammonia (390 ml., *d* 0·885) daily for 7 days in a stoppered bottle. A homogeneous solution was formed which was evaporated in 3 portions at 19 mm. in a water-bath at 78°. The product was dried ($CaCl_2$) to constant weight (65 g.) in a vacuum. A white mass resulted which was broken into small pieces and heated under reflux with methylene chloride (580 ml.), and the solution filtered (warm-water funnel); the residue was similarly extracted with 60 ml. of methylene chloride. Monomeric methacrylamide crystallised from the filtrates on cooling in ice, and two further crops were obtained from the mother-liquor; total yield 48 g. (75%), m. p. range 95—109°. Repeated crystallisation from methylene chloride gave thin plates, m. p. 110—111° (Bruylants and Castille, *loc. cit.*, record m. p. 102—106°) [Found: N, (i) 16·4, (ii) 16·6. Calc. for C_4H_7ON: N, 16·5%].

At the b. p. of the solution, 1·0 g. of methacrylamide was dissolved by 11·4 g. of methylene chloride.

In the above preparation, the ratio of methyl methacrylate (in g.) to ammonia (in ml.) was 1 : 5; similar preparations with ratio 1 : 3 (7 days' reaction) gave (i) 70, (ii) 63% yield, and with ratio 1 : 2 (29 days' reaction) 28% yield.

Polymethacrylamide.—Specimens of polymethacrylamide were characterised by determining the intrinsic viscosity, $[\eta]_c$, of a 1% solution of the polymer in water, a No. 1 B.S.S. Ostwald viscometer being used at 25°.

(A) Methacrylamide (15·0 g.) was dissolved in toluene (61 ml.) in a flask, fitted with a reflux condenser and a mechanical stirrer, immersed in an oil-bath kept (thermo-regulator) at 120° ± 1·5°. A current of nitrogen was passed through the solution. A solution of benzoyl peroxide in toluene was added from a burette fitted to the apparatus; 9 ml. of solution containing 0·36 g. of peroxide were added in 11 portions during 3 hours. After a further ½ hour the reaction mixture was filtered, and the polymer thrice washed by heating it under reflux with 30 ml. of methylene chloride and filtering it off. It was dried to constant weight by repeatedly heating it at 100° and allowing it to cool in a vacuum in the presence of calcium chloride and paraffin wax. The polymethacrylamide so prepared was a fine, white powder, 11·3 g. (75%), $[\eta]_c$ (i) 0·54 (*c*, 0·872), (ii) 0·55 (*c*, 0·874) [Found: N, (i) 15·0, (ii) 14·6%].

(B) Methacrylamide (15·0 g.), dissolved in toluene (45 ml.), was polymerised under the conditions recorded for (A) with catalysis by 0·36 g. of benzoyl peroxide dissolved in 13 ml. of toluene and added in 10 portions during 3 hours; reaction was continued for a further ½ hour. The polymer was washed and freed from solvent as above (11·8 g., 78%); it had $[\eta]_c$ (i) 0·60 (*c*, 0·764), (ii) 0·61 (*c*, 0·899) [Found: N, (i) 14·8, (ii) 15·0%]. This polymer was dissolved in cold water and titrated with sodium hydroxide, with phenolphthalein as indicator; 1·000 g. required (i) 0·53, (ii) 0·55 ml. of 1·000N-sodium hydroxide for neutralisation.

(C) Methacrylamide (15·0 g.), dissolved in toluene (38 ml.), was polymerised under the conditions recorded for (A) with catalysis by 0·38 g. of peroxide dissolved in 7 ml. of toluene and added in 6 portions during 3 hours; reaction was continued for a further ½ hour. The polymethacrylamide was washed and freed from solvent as for (A) (13·3 g., 89%); it had $[\eta]_c$ (i) 0·12 (*c*, 0·919), (ii) 0·12 (*c*, 0·919).

(D) Methacrylamide (10·2 g.), dissolved in ethyl acetate (40 ml.), was polymerised under the conditions recorded for (A) but with the flask immersed in a water-bath at 85°. Polymerisation was catalysed by 0·51 g. of peroxide added in 4 portions during 20 hours. The polymer was washed (20-ml. portions of methylene chloride) and freed from solvent as for (A); 4·6 g. (45%) were obtained, $[\eta]_c$ 0·09 (*c*, 0·950).

Polymethacrylamide has a strong tendency to retain solvents and is hygroscopic. Specimens for analyses and viscosity determinations were further heated at 110° for 1 hour at 12 mm. in the presence of phosphoric oxide; during this treatment a small quantity of monomer separated as a crystalline sublimate, m. p. 110—111°.

Polymethacrylamide (preparation B), dried (P_2O_5) as above, was kept in a "humidor" over saturated aqueous ammonium chloride solution (80% relative humidity) at 13—20° and increased in weight as follows:

Time	4 hrs.	24 hrs.	54 hrs.	8 days	16 days	83 days
Increase, %	12	24	27	29	26	25

The polymer was dissolved in cold water and titrated with sodium hydroxide (phenolphthalein); 1·000 g. (dry) required (i) 0·47, (ii) 0·43 ml. of 1·000N-sodium hydroxide, indicating that there had been no hydrolysis under these humid conditions.

To a solution of polymethacrylamide (preparation C, 1·00 g.) in 10·0 ml. of water were added with stirring, at 32°, 5·0 ml. of methyl alcohol. Polymer was precipitated; it was filtered off, dried ($CaCl_2$) in a vacuum, and weighed 0·58 g. A similar experiment but with 10·0 ml. of methyl alcohol yielded 0·79 g. of polymer. These results indicate a method of fractionation.

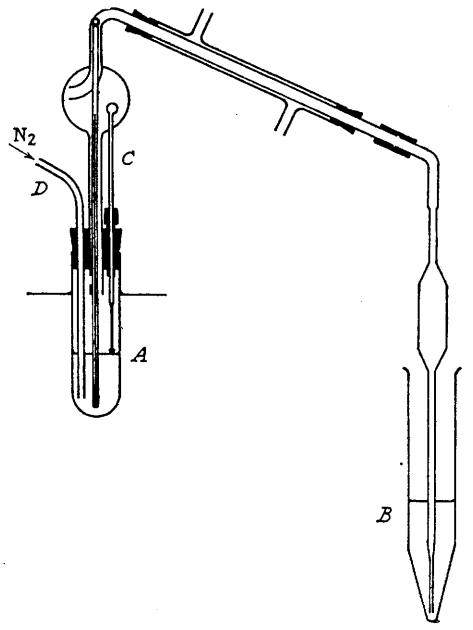
Method for Rates of Hydrolysis.—The amide (approximately 0·01 mole) was weighed into the tube *A* (Fig. 2); the weights taken were:

Expt.	Amide.	Weight, g.	Expt.	Amide.	Weight, g.
i	Acetamide	0·5815	iv	Methacrylamide	0·8503
ii	,, ...	0·6100	v	Polymethacrylamide (B)	0·7764
iii	Methacrylamide	0·8671	vi	,, ,, ...	0·7753

5 Ml. of water and 25 ml. of 2·30N-sodium hydroxide were then added from pipettes. Approximately 75 g. of N/5-sulphuric acid were weighed into the trap *B*. The tube *A* was connected to the rest of the apparatus, and the rod *C* adjusted to touch the surface of the liquid in *A*; *A* was then immersed in an

oil-bath fitted with a stirrer and thermo-regulator and kept at 107° ± 1°. Throughout the experiment a slow stream of nitrogen was passed through the apparatus. At intervals, measured from the time of immersion in the oil-bath, 5 ml. of acid (5·02 g.) were removed by pipette from *B* and titrated with N/4-sodium hydroxide, with methyl-red as indicator. At the end of the experiment, *B* and its contents were weighed as a check on evaporation from or distillation into *B*, and the net weight change was found to be very small. The temperature of the solution in *A* rose to 95° during the first 8 minutes after immersion of *A* in the oil-bath and remained thereafter at 97° ± 2°. The temperature difference between the oil-bath and the solution in *A* was due to the reflux of water between *A* and the anti-splash bulb. After 3 hours, the level of the solution in *A* had fallen slightly owing to evaporation, and sufficient water was added through *D* to restore contact between the surface of the solution and *C*.

FIG. 2.



The various acid contents were calculated in ml. of 1·000N-sulphuric acid; then we have: (millimoles of ammonia evolved at time *t*) = (initial acid content of *B*) − (sum of acid contents of portions withdrawn, for titration, up to *t*) − (acid content of *B* at *t*).

The results obtained for acetamide, methacrylamide monomer, and polymethacrylamide (preparation B) are plotted in Fig. 1.

Polymer recovered from Hydrolysis.—Polymethacrylamide (3·6 g.; preparation B) was dissolved in 24 ml. of water, and a solution of 6·8 g. sodium hydroxide in 22 ml. of water was added. A coagulum was formed which soon dissolved; the solution (3·7N. in NaOH) was heated on a steam-bath for 2 hours. The clear solution was added, with washes, to 40 ml. of 5N-hydrochloric acid, and the whole heated on a steam-bath, cooled in ice, and filtered. The precipitate was thrice washed by suspending it in water, heating on a steam-bath, cooling in ice, and filtering off, and then dried ($CaCl_2$) in a vacuum. It weighed 2·7 g. [Found: N, (i) 4·8, (ii) 5·05%]. This polymer was dissolved in sodium hydroxide, and the solution neutralised to phenolphthalein with sulphuric acid, and it was found that 1·000 g. of polymer neutralised (i) 7·90, (ii) 7·86 ml. of 1·000N-sodium hydroxide.

I thank Dr. J. Kenyon, F.R.S., for his interest in this work, and the D.S.I.R. for a Senior Research Award.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, May 16th*, 1949.]