Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Photolysis of Poly-N-dimethyl-β-amino Ethyl Methacrylate in Aqueous Solutions

H. H. G. Jellinek[a]; C. H. Chou[a]
[a] Department of Chemistry, Clarkson College of Technology, Potsdam, New York

To cite this Article Jellinek, H. H. G. and Chou, C. H.(1970) 'Photolysis of Poly-N-dimethyl-β-amino Ethyl Methacrylate in Aqueous Solutions', Journal of Macromolecular Science, Part A, 4: 1, 255 — 258
To link to this Article: DOI: 10.1080/00222337008060977
URL: http://dx.doi.org/10.1080/00222337008060977

J. MACROMOL. SCI.–CHEM., A4(1), pp. 255-258, January, 1970

LETTER TO THE EDITOR

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SUMMARY

The photolyses of atactic and isotactic polymethacrylic acids, as functions of pH, electrolyte concentration, chain length, and light intensity, have been studied recently [1-3]. Random degradation takes place in either case. The rate constants decrease with increasing pH values.

The photolysis of a polybase is described in this note.

EXPERIMENTAL

All chemicals were of analytical reagent-grade quality. The polymer was prepared according to Voelker [2]. Sulfuric acid (20.8 g, 97%) was added dropwise to a solution of 77.2 g of dimethylaminoethyl methacrylate (Rohm and Haas) in 99.4 g of cooled water. After addition of 0.60 g of potassium persulfate (Fisher, certified reagent), the reaction mixture was refluxed under stirring for 4 hr at 60-70°C. A 50.2% w/v solution of the polymer was obtained. The sample was purified by washing with an acetone-water mixture and then dried in vacuo at 100°C to constant weight. Yield: 75 g.

The apparatus was the same as described previously [1].

PROCEDURE AND RESULTS

Table 1 gives intrinsic viscosities measured at different pH values.

Figure 1 shows $(1/[\eta]_t) - (1/[\eta]_0$ as a function of photolysis time at various pH values as indicated in Table 1 (λ = 2537 Å; total intensity of light source, ca. 3×10^{18} to 5×10^{18} quanta/sec; cylindrical "ultrasil" cell: length, 3 cm; i.d., 4 cm; distance from light source, 5 cm; N_2 passed

Table 1. Intrinsic Viscosities, [η] (dl/g), as a Function of pH Values (Polymer Concentration ca. 0.02% w/v, 25 ± 0.005°C)

Solvent	pH	[η], dl/g, before irradation
1×10^{-1} M HCl	1.0	1.05
B	3.6	1.02
2.5 ml A[a]/97.5 ml B[b]	4.0	0.93
3.0 ml A/97.0 ml B	4.5	0.88
20 ml A/80 ml B	5.7	0.56
30 ml A/70 ml B	6.0	0.45
70 ml A/30 ml B	6.6	0.12
95 ml A/5 ml B	7.5	0.06

[a] A = M/15 Na_2HPO_4,
[b] B = M/15 KH_2PO_4.

through solution; 25 ± 0.05°C). After irradiation the solutions were adjusted to pH 3 with 2×10^{-3} M HCl and diluted with 2×10^{-3} M HCl for intrinsic viscosity measurements.

Rate constants, derived from the slopes of the straight lines in Fig. 1, are shown in Table 2 (polymer concentration, ca. 0.2% w/v; 25 ± 0.05°C).

Table 2

pH	1	3.5	4.5	5.4	6.0	7.8
10^{-1} k(min^{-1} g/100 ml)	2.75	3.45	4.0	3.2	2.9	2.4

The rate constants pass through a maximum, whereas they decrease continuously with increasing pH for the corresponding polyacid. The addition of M/15 Na Cl to the polymer solution had no effect on the photolysis.

The optical absorbance (1 cm) decreases with exposure time at any one pH value. The position of the absorption maximum (215 mμ) does not change with pH; the absorbance changes only slightly (from 0.89 to 0.95). The polyacid has its maximum at about 201 mμ at all pH values; the absorbance decreases slightly with pH (0.64-0.57). The absorbance of the acid also decreases with exposure time at any one pH value.

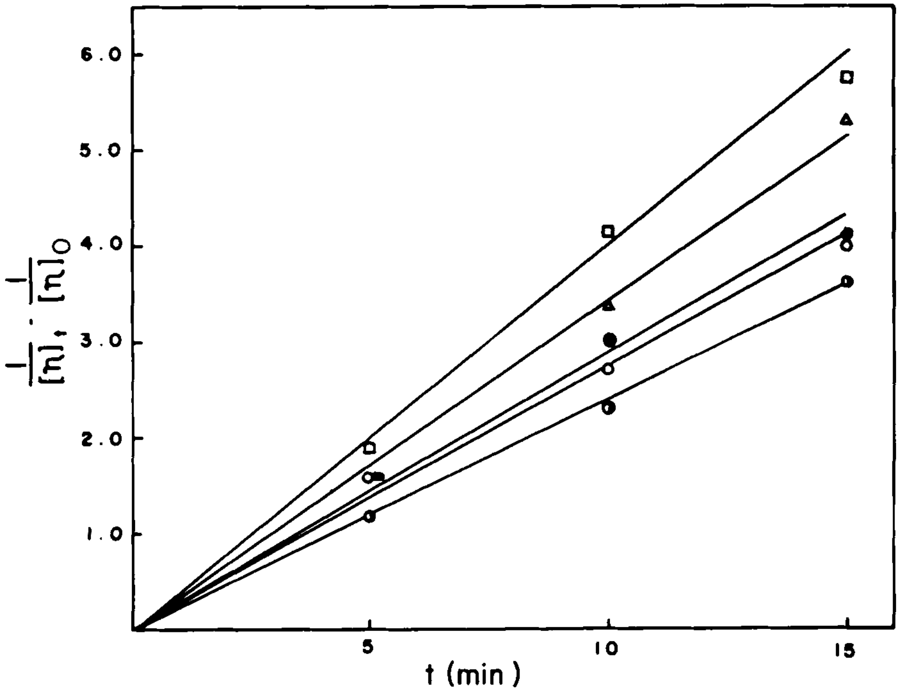
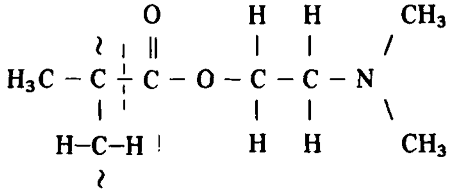


Fig. 1. $(1/[\eta]_t) - (1/[\eta]_0)$ as a function of reaction time at 25°C; pH values: ◑, 7.8; ○, 1.0; ●, 6.0; △, 3.5; □, 4.5.

The primary photolytic process is probably due to light absorption by the carbonyl group; this leads eventually to chain scission:



$$\begin{array}{ccccccccc} & & \mathrm{O} & & \mathrm{H} & & \mathrm{H} & & \mathrm{CH_3}\\ \wr & & \| & & | & & | & & /\\ \mathrm{H_3C}-\mathrm{C} & \vdots & \mathrm{C} & -\mathrm{O}- & \mathrm{C} & - & \mathrm{C} & - & \mathrm{N}\\ | & & & & | & & | & & \backslash\\ \mathrm{H{-}C{-}H} & \vdots & & & \mathrm{H} & & \mathrm{H} & & \mathrm{CH_3}\\ \wr & & & & & & & & \end{array}$$

The rate constants for the photolysis of the polybase are about twice as large at low pH values and about four times larger at high pH values than the corresponding ones for the polyacid.

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H. H. G. Jellinek
C. H. Chou

Department of Chemistry
Clarkson College of Technology
Potsdam, New York

Accepted by editor July 29, 1969
Received for publication July 29, 1969