

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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- $\beta$ -amino Ethyl Methacrylate in Aqueous Solutions

H. H. G. Jellinek<sup>a</sup>; C. H. Chou<sup>a</sup>

<sup>a</sup> 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- $\beta$ -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>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LETTER TO THE EDITOR

## Photolysis of Poly-N-dimethyl- $\beta$ -amino Ethyl Methacrylate in Aqueous Solutions

### 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 ( $\lambda = 2537 \text{ \AA}$ ; total intensity of light source, ca.  $3 \times 10^{18}$  to  $5 \times 10^{18}$  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,  $[\eta]$  (dl/g), as a Function of pH Values (Polymer Concentration ca. 0.02% w/v,  $25 \pm 0.005^\circ\text{C}$ )

Solvent	pH	$[\eta]$ , dl/g, before irradiation
$1 \times 10^{-1}$ M HCl	1.0	1.05
B	3.6	1.02
2.5 ml A <sup>a</sup> /97.5 ml B <sup>b</sup>	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

<sup>a</sup>A = M/15 Na<sub>2</sub>HPO<sub>4</sub>,

<sup>b</sup>B = M/15 KH<sub>2</sub>PO<sub>4</sub>.

through solution;  $25 \pm 0.05^\circ\text{C}$ ). After irradiation the solutions were adjusted to pH 3 with  $2 \times 10^{-3}$  M HCl and diluted with  $2 \times 10^{-3}$  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;  $25 \pm 0.05^\circ\text{C}$ ).

**Table 2**

pH	1	3.5	4.5	5.4	6.0	7.8
$10^{-1}$ k(min <sup>-1</sup> 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 m $\mu$ ) does not change with pH; the absorbance changes only slightly (from 0.89 to 0.95). The polyacid has its maximum at about 201 m $\mu$  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.

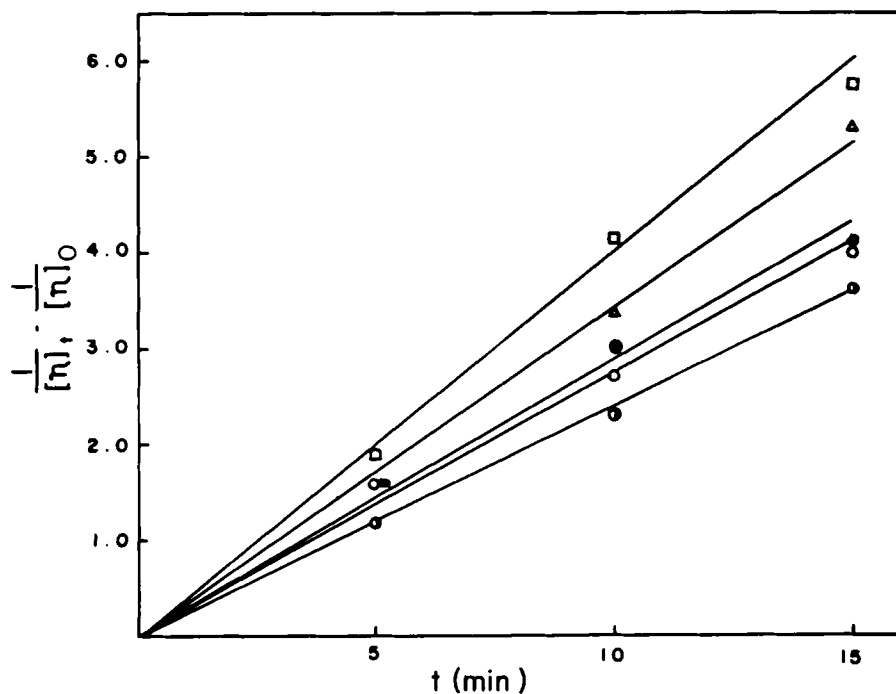
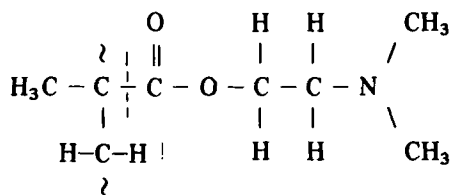


Fig. 1.  $(1/[\eta]_t) - (1/[\eta]_0)$  as a function of reaction time at 25°C; pH values: ○, 7.8; ◊, 1.0; ●, 6.0; △, 3.5; ◻, 4.5.

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



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.

## REFERENCES

- [1] H. H. G. Jellinek and C. H. Chou, *Can. J. Chem.*, **42**, 522 (1964).
- [2] H. H. G. Jellinek and S. N. Lipovac, *Macromol. Chem.*, **1(4)**, 773 (1966).
- [3] H. H. G. Jellinek and S. N. Lipovac, *J. Polymer Sci., Part C*, **22**, 621, (1969).

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*