

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>

### Vinyl Polymerization. 401. Polymerization of Vinyl Monomer Initiated with Poly-2-hydroxyethylmethacrylate

T. Ouchi<sup>a</sup>; M. Moriguchi<sup>a</sup>; A. Kuriyama<sup>a</sup>; M. Imoto<sup>a</sup>

<sup>a</sup> Department of Applied, Chemistry Faculty of Engineering Kansai University Senriyama, Osaka, Japan

**To cite this Article** Ouchi, T. , Moriguchi, M. , Kuriyama, A. and Imoto, M.(1981) 'Vinyl Polymerization. 401. Polymerization of Vinyl Monomer Initiated with Poly-2-hydroxyethylmethacrylate', Journal of Macromolecular Science, Part A, 16: 7, 1251 – 1261

**To link to this Article:** DOI: 10.1080/00222338108063232

**URL:** <http://dx.doi.org/10.1080/00222338108063232>

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.

## **Vinyl Polymerization. 401. Polymerization of Vinyl Monomer Initiated with Poly-2-hydroxyethylmethacrylate**

TATSURO OUCHI, MITSUHISA MORIGUCHI, AKIRA KURIYAMA,  
and MINORU IMOTO

Department of Applied Chemistry  
Faculty of Engineering  
Kansai University  
Senriyama, Suita, Osaka 564, Japan

### **ABSTRACT**

The polymerization of vinyl monomer initiated with poly-2-hydroxyethylmethacrylate (PHEMA) in water was carried out at 85°C. Cu(II) ion was not necessary for this polymerization. Methacrylate monomers were polymerized, while styrene and acrylonitrile were not. The polymerization was found to proceed through a radical mechanism in the interior of PHEMA which was swelled in water. The grafting efficiency of MMA polymer obtained was about 90%. The overall activation energy was estimated to be 32.9 kJ/mol.

### **INTRODUCTION**

In the study on "the so-called uncatalyzed polymerization," we carried out the polymerization of methyl methacrylate (MMA) by starch [1], cellulose [2], and polyvinyl alcohol [3]. These macromolecules with OH groups were found to be able to initiate radical polymerization only in the presence of Cu(II) or Fe(III) ion.

The present paper deals with the radical polymerization of vinyl monomer initiated with poly-2-hydroxyethylmethacrylate (PHEMA). Interestingly, in this case, the polymerization proceeded without Cu(II) ion.

## EXPERIMENTAL

### Materials

**PHEMA.** PHEMA was prepared according to the Gregonis et al. method [4] by the polymerization of 2-hydroxyethylmethacrylate (Mitsubishi Gas Co.). The polymer thus obtained was purified by reprecipitating twice from the ethanol/diethyl ether system and further from the ethanol/ethyl acetate system.

The existence of a peroxide group in PHEMA could not be observed by the KI method. Moreover, it was confirmed by an ESR spectrum that the free radical was not included in the PHEMA obtained.

The number-average degree of polymerization of PHEMA obtained was estimated to be 2200 from the viscosity measured in N,N-dimethylformamide at 25°C by Bohdanecký's equation [5].

### Other Materials

MMA, other monomers, and organic solvents were purified by the usual methods. Water was ion-exchanged and distilled. Copper(II) chloride was of special commercial grade and used without further purification.

### Procedure

Vinyl monomer, PHEMA, and water were placed in a tube. The tube was sealed under vacuum after thawing with nitrogen. The tube was heated at 85°C for a definite time with shaking. The reaction mixture was poured into a large amount of methanol to precipitate the polymerization product. A part of the PHEMA went in the filtrate. This PHEMA was recovered by evaporation of methanol and addition of ethyl acetate. Thus the amount of PHEMA remaining in the product was calculated by subtracting the PHEMA recovered from the PHEMA used in the polymerization. After drying the product under vacuum, the conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{product (g)} - \text{PHEMA remained in product (g)}}{\text{monomer (g)}} \times 100$$

TABLE 1. Polymerization of Vinyl Monomers With and Without PHEMA<sup>a</sup>

Monomer	PHEMA (g)	Conversion (%)
MMA	0	0.59
	0.1	8.23
Ethyl methacrylate	0	0.71
	0.1	5.86
Isopropyl methacrylate	0	0.79
	0.1	6.21
n-Butyl methacrylate	0	0.69
	0.1	5.45
Styrene	0	2.00
	0.1	4.43
Acrylonitrile	0	0
	0.1	0.06

<sup>a</sup> Monomer, 3 cm<sup>3</sup>; H<sub>2</sub>O, 10 cm<sup>3</sup>; 85°C; 3 h; with shaking.

The efficiency of grafting (EG) of MMA onto PHEMA was estimated by extracting homopoly-MMA with benzene for 50 h using a Soxhlet extractor. EG was calculated by the following equation:

$$EG = \frac{\text{total poly-MMA (g)} - \text{homopoly-MMA (g)}}{\text{total poly-MMA (g)}} \times 100$$

## RESULTS AND DISCUSSION

### Polymerization of Vinyl Monomers

The selectivity of vinyl monomers for polymerization by PHEMA is shown in Table 1. Such a selectivity of vinyl monomers can be explained by the concept of "hard and soft hydrophobic areas (HA) and monomers," that is, a monomer, having a definite hardness as a measure of the hydrophobicity, can be most easily incorporated into the HA having a corresponding hardness which is also a measure of hydrophobicity of the HA [6, 7].

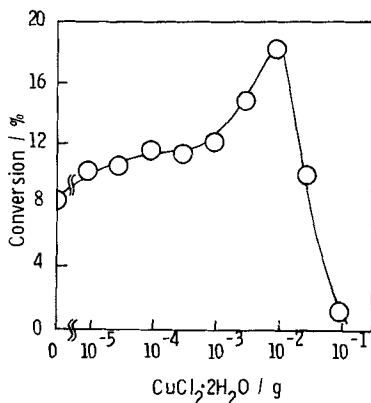


FIG. 1. Conversion of MMA vs weight of copper(II) chloride. MMA, 3 cm<sup>3</sup>; PHEMA, 0.1 g; H<sub>2</sub>O, 10 cm<sup>3</sup>; 85°C; 3 h; with shaking.

### Effect of Cu(II) Ion on Polymerization

The so-called "uncatalyzed radical polymerization" can be classified in two groups. The first group requires the presence of a metallic ion, particularly Cu(II) ion. The polymerizations of MMA initiated with starch [1], cellulose [2], polyvinyl alcohol [3], nylon-3 [8],  $\alpha$ -amylase [9], lysozyme [10], etc. belong to this group. The second group does not require the coexistence of metallic ions. Examples could be obtained, for instance, with sodium polystyrene-sulfonate [12] and sodium poly-p-vinylphenolate [13].

The effect of Cu(II) ion on the conversion of MMA was investigated by shaking MMA, water, and PHEMA in the presence of various amounts of Cu(II) ion. The results obtained are shown in Fig. 1. As can be seen, even when Cu(II) ion was absent, the conversion of 8.23% was observed. Accordingly, it was concluded that the present polymerization belongs to the second group.

### Proof for Radical Mechanism

Into a mixture of 3 cm<sup>3</sup> of MMA, 0.1 g of PHEMA, and 10 cm<sup>3</sup> of H<sub>2</sub>O, 0.1 g of radical scavenger [hydroquinone (HQ), 2,2-diphenyl-1-picrylhydrazyl (DPPH), or 1,3,5-triphenylverdazyl (TPV)] was added and then the system was shaken at 85°C for 3 h. The results, which are listed in Table 2, show that the addition of these radical scavengers inhibits polymerization. Thus it was concluded that the polymerization proceeds through a radical mechanism.

TABLE 2. Effect of Radical Scavenger on the Polymerization of MMA<sup>a</sup>

Radical scavenger	Conversion (%)
None	8.23
HQ	0.89
DPPH	0
TPV	0

<sup>a</sup>MMA, 3 cm<sup>3</sup>; PHEMA, 0.1 g; H<sub>2</sub>O, 10 cm<sup>3</sup>; 85°C; 3 h; with shaking.

### Necessity of Water

Keeping the amounts of MMA and PHEMA constant at 3 cm<sup>3</sup> and 0.1 g, respectively, and varying the amount of water, polymerizations of MMA were carried out with shaking. The results obtained are shown in Fig. 2. As can be seen, the existence of water was indispensable for the polymerization initiated with PHEMA. Conversion of MMA increased with the amount of water up to 1 cm<sup>3</sup> of water, while conversion is independent of the amount of water beyond that amount.

### Phase Where the Polymerization Takes Place

In order to ascertain the phase in which polymerization took place, polymerization was carried out on standing. The reaction tube was allowed to stand at 85°C for 3 h. As shown in Fig. 3, the polymerized system consisted of three phases: a clear MMA layer, a muddy water layer, and the swelled PHEMA. These layers were separately poured into methanol. The conversions seen were 1.02, 0.20, and 5.1% respectively. Thus it is clear that this polymerization takes place in the interior of the clump of PHEMA swelled in water.

### Effect of the Amount of PHEMA on the Polymerization

Polymerization of MMA was carried out in ethanol, acetone, or water with shaking with varying amounts of PHEMA. PHEMA is soluble in ethanol and insoluble in water and acetone. The results obtained are shown in Fig. 4. In the case of water, conversion of MMA increases linearly with the amount of PHEMA. However, in

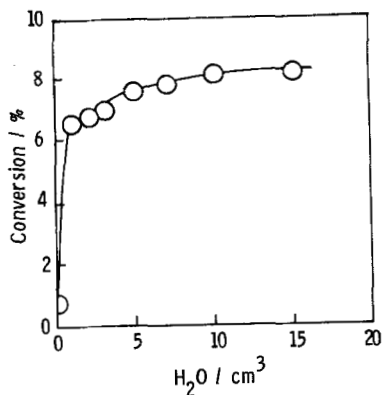


FIG. 2. Amount of water vs. conversion of MMA. MMA, 3 cm<sup>3</sup>; PHEMA, 0.1 g; 85°C; 5 h; with shaking.

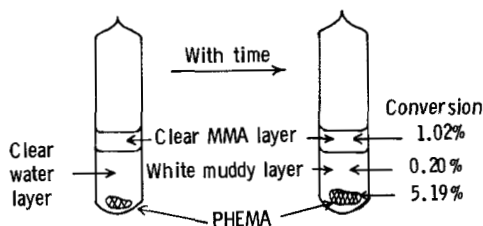


FIG. 3. Polymerization on standing. MMA, 3 cm<sup>3</sup>; PHEMA, 0.1 g; H<sub>2</sub>O, 10 cm<sup>3</sup>; 85°C; 3 h.

the cases of acetone and ethanol, very little polymerization takes place. Accordingly, polymerization takes place only in the swelled phase of PHEMA.

### Efficiency of Grafting

Figure 4 also shows that EG was marvelously large. An EG as large as 90% has never been observed before as far as our literature search reveals.

### Effect of the Amount of MMA on the Yield of Poly-MMA

Polymerization was carried out with shaking while keeping PHEMA and water constant and varying the amount of MMA. The effect of the

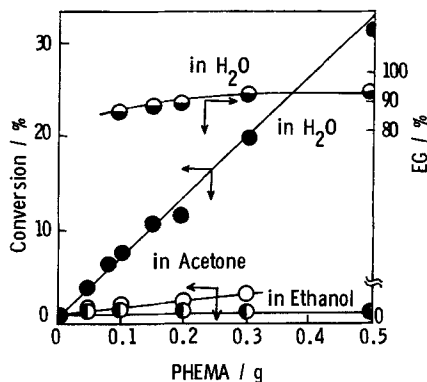


FIG. 4. Effects of amount of PHEMA on the conversion of MMA and EG. MMA,  $3 \text{ cm}^3$ ; solvent,  $10 \text{ cm}^3$ ;  $85^\circ \text{C}$ ; 3 h; with shaking.

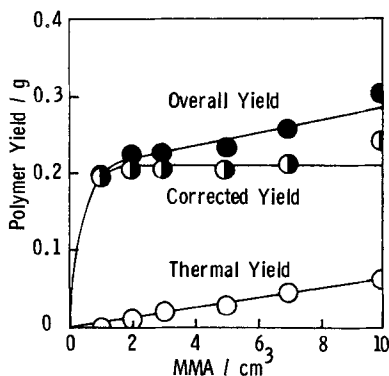


FIG. 5. Effect of the amount of MMA on the polymer yield.  $\text{H}_2\text{O}$ ,  $10 \text{ cm}^3$ ;  $85^\circ \text{C}$ ; 3 h; with shaking. ( $\bullet$ ,  $\circ$ ) PHEMA, 0.1 g; ( $\circ$ ) PHEMA, 0 g.

amount of MMA on the polymer yield in grams is shown in Fig. 5. By subtracting the thermal yield from the overall yield, the corrected yield is obtained. The thermal yield indicates the poly-MMA in grams obtained in the absence of PHEMA. Beyond a certain amount of MMA, the corrected yield became independent of the amount of MMA. This result means that the reaction in the swelled clump of PHEMA was limited.



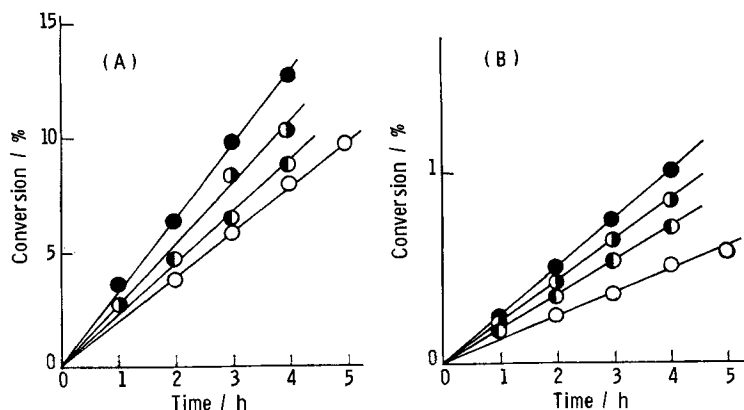


FIG. 6. Time-conversion curves for (A) polymerization in the presence of 0.1 g of PHEMA and (B) polymerization in the absence of PHEMA. MMA, 3 cm<sup>3</sup>; H<sub>2</sub>O, 10 cm<sup>3</sup>; with shaking. (○) 75°C; (◐) 80°C; (●) 85°C; (◉) 90°C.

### Estimation of Overall Activation Energy

Time-conversion curves were obtained by carrying out polymerizations at 75–90°C with a system of 3 cm<sup>3</sup> of MMA and 10 cm<sup>3</sup> of H<sub>2</sub>O in the presence or absence of 0.1 g of PHEMA. The results obtained are shown in Fig. 6. No induction period was observed, and there was a good linear relationship between the conversion and polymerization time. The rate of polymerization ( $R_p$ ) of MMA was calculated by

$$R_p \text{ (g/h)} = \frac{\left( \begin{array}{l} \text{overall poly-MMA obtained} \\ \text{in the presence of PHEMA (g)} \end{array} \right) - \left( \begin{array}{l} \text{poly-MMA obtained in} \\ \text{the absence of PHEMA (g)} \end{array} \right)}{\text{time (h)}}$$

On applying the values of  $R_p$  to the Arrhenius equation (Fig. 7), the overall activation energy was calculated to be 32.9 kJ/mol.

### A Proposed Mechanism of Polymerization

In 1968, Kinoshita et al. [14] reported that some cross-linked polymers could polymerize MMA without any initiator and solvent. Their reasoning was that the bond fission of the cross-linked polymer-gels occurred through the swelling of the net-structure which produced

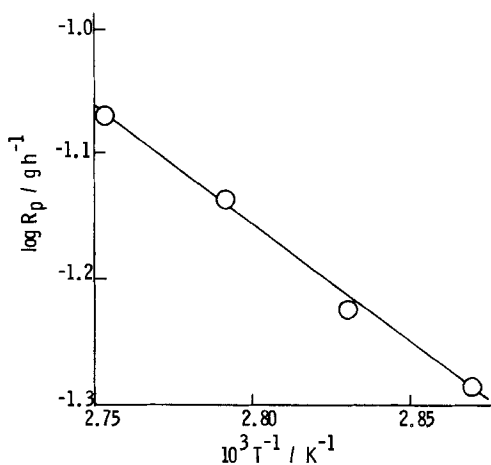


FIG. 7. Arrhenius plots.

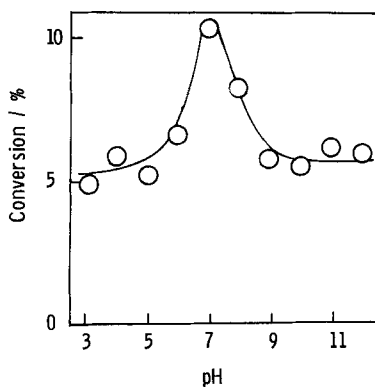


FIG. 8. Conversion of MMA vs pH of aqueous solution. MMA, 3 cm<sup>3</sup>; PHEMA, 0.1 g; buffer solution, 10 cm<sup>3</sup>; 85°C; 3 h; with shaking. The buffer solution was as follows: pH 3-4,  $\underline{M}/10$  sodium citrate- $\underline{M}/10$  HCl; pH 5-6,  $\underline{M}/10$  sodium citrate- $\underline{M}/10$  NaOH; pH 10-12,  $\underline{M}/20$  Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>- $\underline{M}/20$  NaOH.

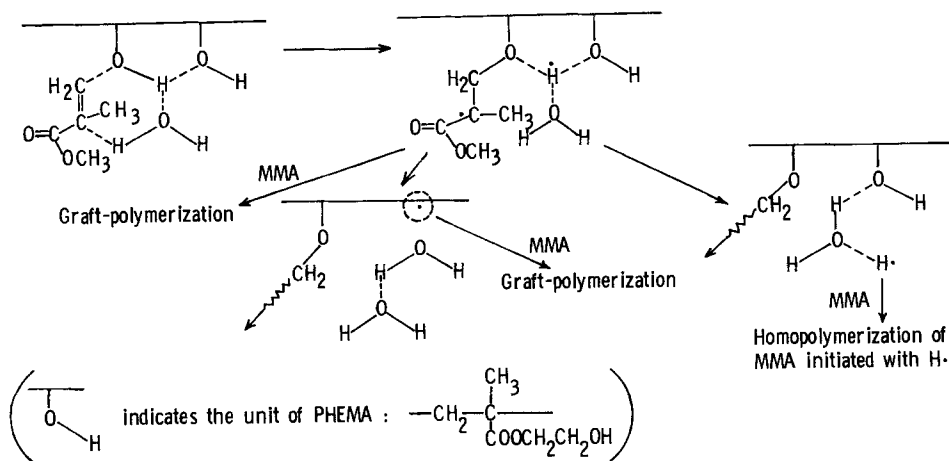


FIG. 9. Initiation mechanism of the radical polymerization of MMA with the system of PHEMA and water.

free radicals. The case of the present paper differs from these because PHEMA is not cross-linked. PHEMA incorporates water and MMA molecules and swells. In the interior of the swelled clump of PHEMA, which is called hydrophobic areas (HA) by the present authors, radical initiation occurs. As mentioned above, the co-existence of water is necessary. Based on the formerly proposed mechanism [3] which was assigned to the uncatalyzed polymerization of MMA by polyvinyl alcohol, we suggest the initiation mechanism by PHEMA as written in Fig. 9.

In this mechanism, the occurrence of  $\text{H}^\bullet$  is assumed. Nakaya et al. [15] calculated the stabilization energy of  $\text{H}^\bullet$  by the LCAO MO method when the  $\text{H}^\bullet$  was surrounded by three O-H groups, and they concluded that the energy amounted to 109 kJ/mol.

The present paper reports that the EG of MMA onto PHEMA is a surprising 90%. Such a large EG can be explained by the above mechanism.

It is concluded that the rate of polymerization is most favored at pH 7. This conclusion can also be supported by the above mechanism; the OH group of PHEMA should exist freely and be untouched by  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions.

## REFERENCES

- [1] M. Imoto, K. Ree, T. Nakaya, and T. Ouchi, *Nippon Kagaku Kaishi*, p. 1560 (1973).
- [2] M. Imoto, S. Otsuka, and T. Ouchi, *Chem. Lett.*, p. 385 (1972).

- [ 3 ] M. Imoto, K. Takemoto, and T. Otsuki, Makromol. Chem., **104**, 244 (1967).
- [ 4 ] D. E. Gregonis, G. A. Russell, and J. D. Andrade, Polymer, **19**, 1279 (1978).
- [ 5 ] M. Bohdanecký, Z. Tuzar, M. Štoll, and R. Chromeček, Collect. Czech. Chem. Commun., **33**, 4104 (1968).
- [ 6 ] M. Imoto, T. Ouchi, E. Morita, and T. Yamada, Nippon Kagaku Kaishi, p. 333 (1980).
- [ 7 ] M. Imoto, T. Ouchi, M. Sakae, E. Morita, and T. Yamada, Modification of Polymers (ACS Symp. Ser., 121), 1980, p. 104.
- [ 8 ] T. Ouchi, T. Nishimura, and M. Imoto, J. Polym. Sci., Polym. Chem. Ed., **14**, 2695 (1976).
- [ 9 ] M. Imoto, N. Sakade, and T. Ouchi, Ibid., **15**, 499 (1977).
- [ 10 ] T. Ouchi, T. Yoshikawa, and M. Imoto, J. Macromol. Sci.-Chem., **12**, 1523 (1978).
- [ 11 ] M. Imoto, Y. Nakamura, and T. Ouchi, Bull. Chem. Soc. Jpn., **49**, 1342 (1976).
- [ 12 ] T. Ouchi, H. Suzuki, T. Yamada, and M. Imoto, J. Makromol. Sci.-Chem., **A12**, 1461 (1978).
- [ 13 ] M. Imoto, M. Inamura, A. Kobayashi, and T. Ouchi, J. Polym. Sci., Polym. Chem. Ed., Submitted.
- [ 14 ] M. Kinoshita, Y. Iki, and M. Imoto, Mem. Fac. Eng., Osaka City Univ., **10**, 173 (1968).
- [ 15 ] T. Nakaya, H. Sutoh, K. Takemoto, and M. Imoto, Kogyo Kagaku Zasshi, **70**, 1949 (1967).

Accepted by editor October 27, 1980

Received for publication December 8, 1980