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. 287. Polymerization of Methyl Methacrylate Initiated by the Polyacrylonitrile-Water-Cupric Ion System

Horng-San Tang[a]; Masayoshi Kinoshita[a]; Minoru Imoto[ab]
[a] Faculty of Engineering, Osaka City University Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan [b] Faculty of Engineering, Kansai University, Suita, Osaka, Japan

To cite this Article Tang, Horng-San , Kinoshita, Masayoshi and Imoto, Minoru(1973) 'Vinyl Polymerization. 287. Polymerization of Methyl Methacrylate Initiated by the Polyacrylonitrile-Water-Cupric Ion System', Journal of Macromolecular Science, Part A, 7: 4, 831 — 843

To link to this Article: DOI: 10.1080/00222337308061175

URL: http://dx.doi.org/10.1080/00222337308061175

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.

J. MACROMOL. SCI.—CHEM., A7(4), pp. 831-843 (1973)

Downloaded At: 10:18 25 January 2011

Vinyl Polymerization. 287. Polymerization of Methyl Methacrylate Initiated by the Polyacrylonitrile-Water-Cupric Ion System

HORNG-SAN TANG, MASAYOSHI KINOSHITA,
and MINORU IMOTO*

Faculty of Engineering
Osaka City University
Sugimoto-cho, Sumiyoshi-ku
Osaka, Japan

ABSTRACT

Methyl methacrylate was found to be polymerized by the system polyacrylonitrile-water-cupric ion without any added initiator. Addition of carbon tetrachloride to this system greatly increased the polymerization rate. Acrylonitrile and styrene did not polymerize in this system. The kinetic behavior of polymerization was the same as the system consisting of cellulose or nylon instead of polyacrylonitrile. When the flaky polyacrylonitrile was swelled or dissolved by the solvent DMF, the conversion and the degree of polymerization of the polymethyl methacrylate formed decreased markedly. Commercial acrylic fiber also initiated polymerization but the activity was lower than with flaky polyacrylonitrile, even after steam treatment, because of the poor permeability of monomer into the fiber.

---

*Present address: Faculty of Engineering, Kansai University, Senriyama, Suita, Osaka, Japan.

Copyright © 1973 by Marcel Dekker, Inc. All Rights Reserved. Neither this work nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Downloaded At: 10:18 25 January 2011

INTRODUCTION

Much work on the polymerization of methyl methacrylate in the presence of added polymers without any initiator has been reported in the past several years [1]. The polymers to be added in these polymerization systems were found to be those which have a hydroxyl group available, such as cellulose and starch, or an amide group, such as nylon and silk. Besides the added polymer, the system needs a slight amount of water and a trace amount of some metal ions, especially cupric or ferric ion [2]. Moreover, carbon tetrachloride greatly promotes the polymerization, sometimes increasing the rate tenfold [3].

From the kinetic behavior of polymerization the initiating species were believed to be metal ion complexes coordinated by hydroxy or amide groups under the cocatalytic interference of water and monomer, either acrylic or methacrylic esters. The ionic valence states of the metal ions, however, did not change during polymerization. Thus the activity of these systems may be compared with the catalytic action of enzymes.

From this standpoint other polymers having polar side groups which are able to coordinate with metal ions may act as active supports for these polymerization systems.

This paper reports on the utility of polyacrylonitrile as an active polymer in the system polymer-water-metal ion and on the kinetic behavior of the polymerization of methyl methacrylate initiated by the above system. The discussion is directed to other elementary reaction steps rather than initiation. The fact that any low molecular weight model compounds of the added polymers could not actively initiate the polymerization suggests the presence of an active species for initiation in polymer matrices. On the other hand the increase of solution viscosity by the addition of inert polymers could not by itself initiate the polymerization. This may show the importance of polymer effects in the initiation step, but the collaboration of a gel effect in the termination step must also be considered [4]. Ceresa and co-workers have already reported on this problem in the polymerization of vaporized methyl methacrylate in the presence of acrylic fiber [5]. This paper shows the possibility of gel-effected rapid polymerization of methyl methacrylate in addition to initiation in polymer matrices.

EXPERIMENTAL

Materials

Methyl methacrylate, carbon tetrachloride, DMF, and benzene were purified as described in a previous paper [6]. Polyacrylonitrile was prepared by the polymerization of acrylonitrile with azobisisobutyronitrile in DMF solution at 60°C and reprecipitated from DMF/methanol before use.

Procedures

Polyacrylonitrile, water, and monomer were pipetted into a glass tube with a bulb in one end. The contents of the tube were frozen and evacuated three times and sealed under a pressure of 10^{-3} Torr. Carbon tetrachloride was also pipetted into the glass tube. Cupric ion was previously adsorbed to polyacrylonitrile by dipping the polymer in cupric salt solution or added directly into the glass tube as an aqueous solution.

Polymerization was carried out shaking the tube in the dark in a thermostat. After a definite time the contents were poured into a large amount of methanol to precipitate the polymer mixtures. The conversion was calculated from the weight increase of the polymer mixture minus the weight of added polyacrylonitrile. Polymethyl methacrylate was extracted with boiling benzene.

Downloaded At: 10:18 25 January 2011

RESULTS AND DISCUSSION

Behavior of Polymerization

A typical time-conversion curve for the polymerization of MMA initiated by the system of PAN, carbon tetrachloride, water, and cupric ion is shown in Fig. 1. The heterogeneous polymerization system consisting of the MMA-carbon tetrachloride mixture, the water layer, and the PAN precipitate became turbid in first hour, showing the progress of polymerization. The conversion of MMA

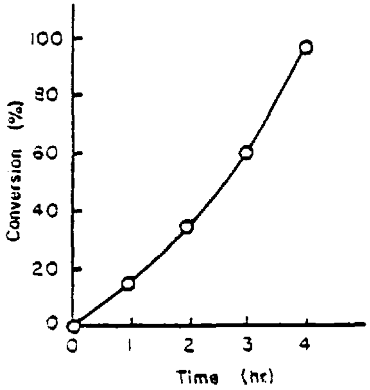

FIG. 1. A typical time-conversion curve for the polymerization of MMA in the presence of PAN. PAN, 0.2 g; MMA, 2 ml; CCl_4, 0.2 ml; water, 10 ml; Cu^{2+}, 10^{-3} g; 85°C.

Downloaded At: 10:18 25 January 2011

to PMMA reached about 95% in 4 hr at a polymerization temperature of 85°. PMMA precipitated as a jelly mass contaminated with PAN.

Necessity of Cu^{2+} and the Accelerating Effect of Carbon Tetrachloride

Table 1 shows the polymerization results obtained under various conditions. The system needs the coexistence of Cu^{2+} to initiate the polymerization of MMA effectively, and the presence of carbon tetrachloride highly accelerates the polymerization rate. As shown in a previous paper, the presence of a polymer matrix and water is also necessary [6]. PAN samples which were dipped in cupric salt solution to adsorb Cu^{2+} ion showed a much higher activity than those to which cupric salt was added as an aqueous solution. The actual concentration of Cu^{2+} adsorbed on PAN could not be determined because the amount was too small to analyze by the usual method.

Effect of the Amount of Carbon Tetrachloride

Figure 2 shows the effect of the amount of carbon tetrachloride on the polymerization rate at 4 hr conversion. Addition of 0.2 ml of carbon tetrachloride caused about a twofold acceleration, but

Downloaded At: 10:18 25 January 2011

TABLE 1. Effect of the Addition of Cu^{2+}

PAN (g)	Carbon tetrachloride (ml)	Water (ml)	Cu^{2+} (g)	Conversion[a] Run 1 (%)	Conversion[a] Run 2 (%)
0.2				9.6, 11.0	8.9
0.2	0.2			10.4, 3.5	8.9, 7.0
0.2		10		5.0	8.2, 8.3
0.2	0.2	10		5.6, 4.7	9.5, 7.9
0.2	0.2	10	Dip[b]	40.7	41.0
	0.2	10	10^{-4} [c]	4.1, 3.8	
0.2	0.2		Dip	4.4, 5.6	
0.2	0.2	10	10^{-4}	15.4, 18.0	20.2
0.2		10	10^{-4}	21.1, 24.9	23.0, 17.3
0.2		10	Dip	16.8, 15.7	22.6, 20.5

[a] PAN sample was dipped in 10 g/liter $CuCl_2$ aqueous solution for 40 hr at room temperature.

[b] Based on Cu^{2+}.

[c] MMA 2.0 ml, 85°, 4 hr.

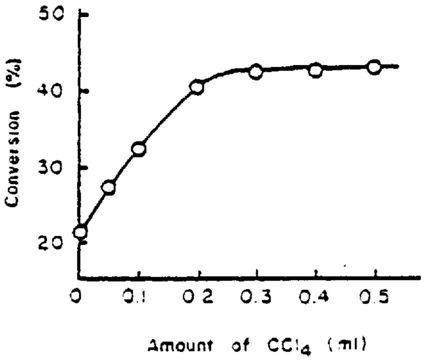

FIG. 2. Amount of CCl_4 vs conversion. PAN, 0.2 g; MMA, 2 ml; water, 10 ml; dipped in Cu^{2+} solution, 85°C, 4 hr.

Downloaded At: 10:18 25 January 2011

an amount over 0.2 ml had no effect under these conditions. The relative amount of carbon tetrachloride to PAN may be decreased in work on a large scale.

Effect of the Amount of PAN

As shown in Table 1, the presence of PAN is necessary to initiate polymerization. The conversion increases with the amount of PAN (Fig. 3), suggesting the presence of active sites on PAN, and 0.3 g of PAN is sufficient to obtain 100% conversion under these conditions. This corresponds to a weight increase of about 800%.

Dependence on the Amount of Cu^{2+}

Figure 4 shows the effect of the amount of Cu^{2+} added to the polymerization system. The most appropriate concentration of Cu^{2+} lies between $10^{-3} \sim 10^{-2}$ g, 10 ml of water. The retardation of polymerization at concentrations of Cu^{2+} higher than 10^{-2} may be due to the presence of free Cu^{2+} in the water layer or on the PAN surface. These results coincide with those obtained with cellulose, nylon, and silk [3, 7, 8].

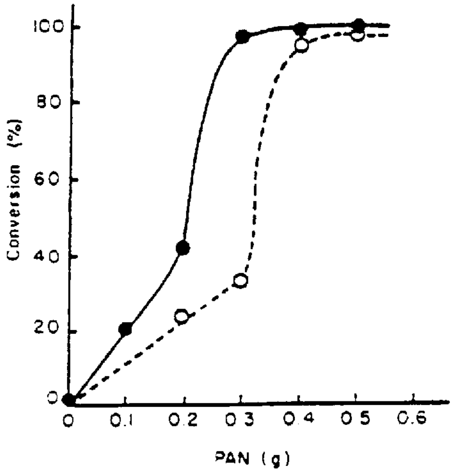

FIG. 3. Amount of PAN vs conversion. (——) CCl_4 present. (- -) CCl_4 absent. MMA, 2 ml; CCl_4, 0.2 ml; water, 10 ml; dipped in Cu^{2+} solution; 85°C; 4 hr.

Downloaded At: 10:18 25 January 2011

Amounts of MMA and Water

The weight of precipitated polymer mixture increases with the amount of MMA (Fig. 5), but saturation is reached at 1 ml of MMA to 0.2 g PAN. This shows that only a small amount of monomer coats the PAN, and that the excess part of monomer, which exists apart from the PAN precipitate, gradually penetrates the surface and diffuses on the inside of the PAN.

The amount of water has a characteristic effect on the polymerization rate as shown in Fig. 6. A very small amount of water shows an excellent catalytic ability. The excess part of water may separate the monomer from the PAN and reduce the diffusion of monomer to PAN surface, and thus the polymerization rate.

Negative Ions

Besides Cu^{2+}, Fe^{3+} has catalytic activity in this polymerization system. Negative ions of cupric salts have no effect on conversion,

Downloaded At: 10:18 25 January 2011

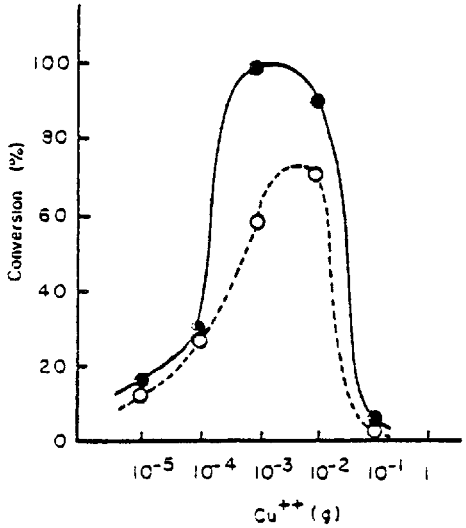

FIG. 4. Conversion vs amount of cupric ion. (——) CCl_4 present. (- -) CCl_4 absent. PAN, 0.2 g; MMA, 2 ml; CCl_4, 0.2 ml; water, 10 ml; 85°C; 4 hr.

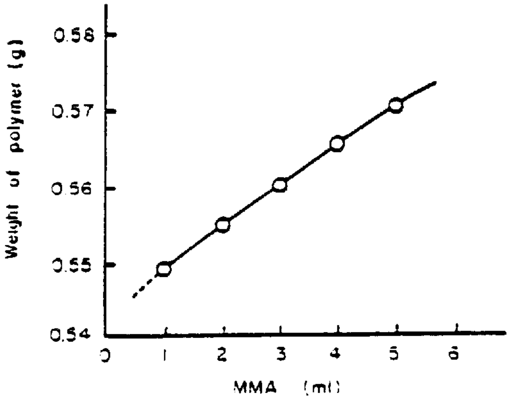

FIG. 5. Effect of amount of MMA on conversion. PAN, 0.2 g; CCl_4, 0.2 ml; water, 10 ml; Cu^{2+}, 10^{-4} g; 85°C; 4 hr.

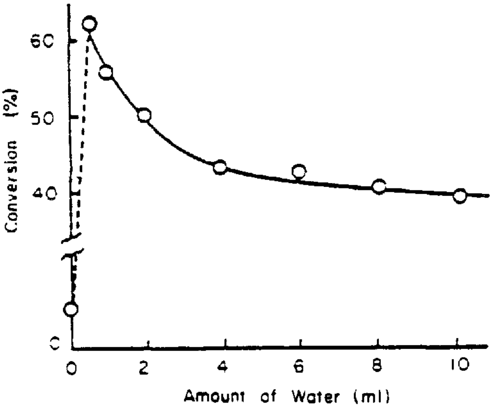

FIG. 6. Effect of amount of water. PAN, 0.2 g; MMA, 2 ml; CCl_4, 0.2 ml; dipped in Cu^{2+} solution; 85°C; 4 hr.

Downloaded At: 10:18 25 January 2011

as shown in Table 2. The active sites for initiation could be metal ion complexes coordinated partly with nitrile groups on the polymer side chain and partly with water.

TABLE 2. Effect of Negative Ions

Salt[a]	Conversion (%)[b]
-	5,6, 4.7
$Cu(NO_3)_2$	28,8, 26.0
$CuSO_4$	27.1, 25.2
$CuBr_2$	28.0, 30.4
$CuCl_2$	29.8, 29.2

[a] Cupric salt which contains 10^{-4} g of Cu^{2+} was added to the polymerization system.

[b] PAN 0.2 g, MMA 2 ml, CCl_4 0.2 ml, water 10 ml, 85°, 4 hr.

Adsorption of Cu^{2+} on PAN was confirmed by ESR measurement. Figure 7 shows ESR spectra of a PAN sample before and after being dipped in cupric salt solution.

FIG. 7. ESR spectra of PAN sample. (- -) Before and (——) after the adsorption of Cu^{2+}.

Downloaded At: 10:18 25 January 2011

Polymerization in the Presence of Acrylic Fiber

Commercial acrylic fiber (PAN fiber) also initiates activity, as shown in Table 3, but the polymerization rate was smaller than that for PAN flakes. This is because of the rigid fiber structure which prevents the penetration of Cu^{2+}, water, carbon tetrachloride, and monomer. When PAN fiber was treated with steam at 150°C for 10 min, and DMF was added to the system as solvent, the conversion was somewhat improved. When PAN fiber was reprecipitated from DMF solution as amorphous flakes, the rate was, of course, much increased.

Polymerization of Acrylonitrile and Styrene

Table 4 shows the polymerization results of acrylonitrile and styrene initiated by the system PAN, Cu^{2+}, water, and carbon tetrachloride.

TABLE 3. Effect of Polymerization Condition

PAN fiber (g)	Water (ml)	DMF (ml)	Cu^{2+} (g)	Conversion[a] (%)
0.2	10		10^{-4}	13.8, 15.6
0.2 (A)[b]	10		10^{-4}	21.4, 21.9
0.2	2.0	2.0	10^{-3}	22.1, 23.5
0.2	2.0	5.0	10^{-3}	22.5, 24.0
0.2 (B)[c]	2.0	5.0	10^{-3}	
0.2 (A)	2.0	5.0	10^{-3}	

[a] MMA 2.0 ml, carbon tetrachloride 0.2 ml, 85°, 4 hr.

[b] PAN fiber was reprecipitated from DMF solution with methanol.

[c] PAN fiber was treated with steam at 150° for 10 min.

TABLE 4. Polymerization of Acrylonitrile and Styrene

Monomer	PAN (g)	CCl_4 (ml)	Water (ml)	Cu^{2+} (g)	DMF (ml)	Conversion[a] (%)
Acrylonitrile	0.2	0.2	5	10^{-4}	10	10.7, 11.3
	0.3	0.2	2	10^{-3}	8	11.2, 10.3
	0.4	0.4	2	10^{-2}	5	11.8, 12.0
Styrene	0.2	0.2	5	10^{-4}	10	9.6, 9.9
	0.3	0.2	2	10^{-3}	8	5.2, 4.8
	0.4	0.4	2	10^{-2}	5	4.3, 3.2

[a] Monomer 2 ml, 85°, 4 hr.

Downloaded At: 10:18 25 January 2011

Downloaded At: 10:18 25 January 2011

TABLE 5. Extraction of Polymethyl Methacrylate

Polymerization condition[a]					Unextracted[b] PMMA (%)	$[\eta]$ of extracted PMMA	$\overline{DP}$ of extracted PMMA
CCl_4 (ml)	Water (ml)	Cu^{2+} (g)	DMF (ml)	Conversion (%)			
0.2	2	10^{-4}	5	75	17.8	1.21	2,800
0.2	2	10^{-4}	15	33	17.8	0.34	540
0.2	10	Dip[c]	0	41	40.0	3.1	9,800
0	10	Dip	0	23	82.0	3.2	10,200

[a] MMA 2 ml, 85°, 4 hr.

[b] After the extraction with benzene at 80° for 30 hr.

[c] PAN sample was dipped in 10 g/liter $CuCl_2$ aqueous solution for 40 hr at room temperature.

Extraction of Polymethyl Methacrylate

Extraction of the PAN-PMMA mixture with boiling benzene gave up to 80% extracts based on PMMA. The extracts were confirmed to be PMMA by elementary analysis (Table 5). The molecular weights of the extracted PMMA reached to one million. When DMF was added to the system as solvent, the molecular weight of the extracted PMMA significantly decreased according to the amount of DMF. This may be attributed to the chain transfer reaction caused by the DMF. A decrease of the conversion by the addition of DMF can be understood by a diffusion controlled termination in the polymer matrix.

ACKNOWLEDGMENT

The authors thank Toho Beslon Co. for the offer of samples of acrylic fiber.

REFERENCES

[1] M. Imoto, K. Takemoto, and H. Stoh, Makromol. Chem., 110, 31 (1967).
[2] M. Imoto, Y. Iki, M. Kinoshita, and K. Takemoto, Makromol. Chem., 122, 287 (1969).
[3] M. Imoto, Y. Iki, Y. Kawabata, and M. Kinoshita, Makromol. Chem., 140, 281 (1970).
[4] M. Kinoshita, Y. Iki, and M. Imoto, Mem. Fac. Eng. Osaka City Univ., 10, 173 (1968).
[5] R. J. Ceresa, J. Polym. Sci., 53, 9 (1961).
[6] M. Imoto, M. Kinoshita, and Y. Iki, J. Macromol. Sci.—Chem., A5(2), 287 (1971).
[7] K. Ueno, M. Kinoshita, and M. Imoto, Kogyo Kagaku Zasshi, 74, 1921 (1971).
[8] H-S. Tang, Y. Kawabata, M. Kinoshita, and M. Imoto, Makromol. Chem., In Press.

Received for publication October 10, 1972

Downloaded At: 10:18 25 January 2011