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

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To cite this Article Imoto, Minoru , Kushibe, Seigo and Ouchi, Tatsuro(1977) 'Vinyl Polymerization. 355. Polymerization of Methyl Methacrylate Initiated with the System Oxycellulose, Cu(II) Ion, and Water', Journal of Macromolecular Science, Part A, 11: 2, 321 — 335

To link to this Article: DOI: 10.1080/00222337708061271

URL: http://dx.doi.org/10.1080/00222337708061271

J. MACROMOL. SCI.–CHEM., A11(2), pp. 321-335 (1977)

Vinyl Polymerization. 355. Polymerization of Methyl Methacrylate Initiated with the System Oxycellulose, Cu(II) Ion, and Water

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ABSTRACT

The polymerization of methyl methacrylate (MMA) initiated with a system of oxycellulose, $CuCl_2$, and water was carried out. The conversion of MMA and the degree of polymerization of homopoly-MMA were larger than obtained with the initiator system of cellulose, $CuCl_2$ and water, while the efficiency of grafting was almost the same. It was confirmed that the polymerization proceeds through a radical mechanism. The effects of amounts of cupric chloride, water, and MMA in the feed on the conversion were studied. The pH of the water phase showed a remarkable effect: maximum conversion was obtained at neutral pH. At 90°C, a ceiling temperature was observed. The overall activation energy was estimated to be 96.7 kJ/mole. The initiation mechanism is discussed.

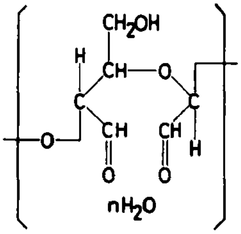
INTRODUCTION

In 1962, Kimura, Takitani, and Imoto [1] found that water-soluble starch can initiate the polymerization of methyl methacrylate (MMA) in the absence of an ordinary radical initiator, i.e., a heterogeneous mixture of starch, water, and MMA led to a conversion of 67.5% of MMA at 85° C. However, when dialdehyde starch was used instead of ordinary starch, the conversion increased to 95%.

Gaylord et al. [2] carried out the polymerization of MMA with ceric ion in the presence of cellulose and concluded that the complex (of cellulose, monomer, and water) containing ceric ion is anchored on the cellulose matrix generated by the interaction of ceric ion with a carbonyl group which is present initially or generated by the cellulose-ceric ion redox reaction. His conclusion seemed to agree with the results obtained by Imoto and his co-workers. Moreover, Gaylord et al. found that glycolaldehyde and glycerinaldehyde have somewhat strong promoting ability for the polymerization of MMA, especially in the presence of cellulose.

Recently, Imoto, Oishi, and Ouchi reported that poly(styrene-co-acrolein) [3] and poly(styrene-co-methyl vinyl ketone) [4] could initiate radical polymerization of vinyl monomers, especially, of MMA, in the absence of cupric ion. It was found also that on reduction of poly(styrene-co-acrolein) with sodium tetrahydroborate, the polymer became inactive for initiation of the polymerization. Thus the peculiar effect of carbonyl group on the polymerization of vinyl monomers became an interesting problem for the so-called "uncatalyzed" polymerization.

The present paper is concerned with the polymerization of MMA initiated by oxycellulose (I) instead of cellulose [4-6] which was used



I

repeatedly as the macromolecular initiator in uncatalyzed polymerization.

EXPERIMENTAL

Materials

Cellulose (regular viscose staple from Toho Rayon Co., $\overline{P}_n$ 300, no content of TiO_2) was purified by Soxhlet extraction with acetone-benzene(1:1 by volume) for 20 hr.

Oxycellulose was prepared by steeping 40 g of purified rayon staple in a solution of 80 g of $HIO_4 \cdot 2H_2O$ in 2.4 dm^3 of water at room temperature for 7 days. After washing with water until the washed water did not color with sodium thiosulfate, the oxycellulose was dried under vacuum.

Analysis. Calcd for $C_6H_8O_5 \cdot H_2O$: C, 40.4%; H, 5.6%. Found for OC-3: C, 38.6%; H, 5.3%. Found for OC-4: C, 39.0%; H, 5.7%.

Here, OC-3 and OC-4 denote different oxycellulose samples. IR spectra of OC-3 and OC-4 were identical to those reported by Rowen et al. [7]. Analyses for C=O, COOH, and peroxide groups were carried out by the methods of oximation [8], titration [9], and potassium iodide, respectively; the results obtained are listed in Table 1.

OC-3, which has a smaller content of COOH, was used principally as the oxycellulose. MMA was purified by the usual methods. Water was ion-exchanged and distilled. $CuCl_2 \cdot 2H_2O$ was of pure commercial grade and used without further purification.

Procedures

The reaction was carried out in a sealed glass ampoule. Oxycellulose (or cellulose) and an aqueous solution of cupric chloride were

TABLE 1. Analyses of Oxycellulose

Oxycellulose	COOH (%)[a]	C=O (%)[b]	Peroxide (%)
OC-3	2.50	106.0	0
OC-4	30.30	115.2	0

[a] Content of COOH per C_6 unit.

[b] Content of 2(C=O) per C_6 unit. Contents over 100% mean that CH_2OH converted into CHO, the glycoside linkage being destroyed to generate new CHO group.

placed in a tube. The tube was flushed with nitrogen, stoppered tightly and allowed to stand at 30-40° C for 24 hr. Then MMA was added and the ampoule was then flushed with nitrogen, frozen, evacuated at 0.1 Torr, and sealed.

The polymerization was carried out with shaking in a thermostat at 85° C, the ampoule was broken, and the contents were poured into a large amount of methanol to precipitate the polymer formed. The polymer was filtered, washed thoroughly with methanol, and dried under vacuum. The monomer conversion was calculated from the relationship (1).

$$\text{Conversion (\%)} \;/\; \frac{\text{Products (g)} - \text{Oxycellulose (g)}}{\text{Monomer (g)}} \times 100 \qquad (1)$$

Homopolymer of MMA was isolated by extracting with benzene for 70 hr using Soxhlet extraction. Efficiency of grafting (EG) was calculated by Eq. (2).

$$\text{EG (\%)} = \frac{\text{Total Polymer (g)} - [\text{Extracted Polymer} + \text{Oxycellulose}]\text{ (g)}}{\text{Polymerized MMA (g)}} \times 100 \qquad (2)$$

In order to evaluate EG, the relationship between the apparent grafting efficiency and extraction time with benzene was observed (Fig. 1). Figure 1 shows that 70 hr is a sufficient period of time for extraction.

MMA homopolymer was recovered from the benzene extract by pouring into methanol. The degree of polymerization $\overline{P}_n$ of MMA homopolymer was calculated from the intrinsic viscosity (benzene, 30°C) by Welch's equation [10].

RESULTS AND DISCUSSION

Comparison of the Initiating Activity of Oxycellulose and Cellulose

Table 2 compares oxycellulose with cellulose in initiating activity. The relationships between the amounts of cupric chloride used and the

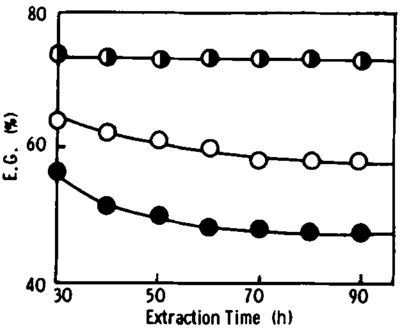


FIG. 1. Grafting efficiency vs. time of extraction with benzene: (◑) 3 cm^3 MMA, 0.1 g OC-3, 10 cm^3 H_2O, 2.1 × 10^{-3} g $CuCl_2 \cdot 2H_2O$, 52.6% conversion; (○) 3 cm^3 MMA, 0.1 g OC-3, 10 cm^3 H_2O, 1.0 × 10^{-2} g $CuCl_2 \cdot 2H_2O$, 13.1% conversion; (●) 4 cm^3 MMA, 0.1 g OC-3, 9 cm^3 H_2O, 1.0 × 10^{-2} g $CuCl_2 \cdot 2H_2O$, 15.2% conversion.

TABLE 2. Comparison of Activities of Oxycellulose with Cellulose for the Polymerization of MMA[a]

$CuCl_2 \cdot 2H_2O$ (g)	Conversion of MMA (%)		EG (%)		$\bar{P}_n \times 10^{-4}$ of homopoly-MMA	
	OC-3	Cellulose	OC-3	Cellulose	OC-3	Cellulose
1.0 × 10^{-1}	0.7	0.2	–	–	–	–
1.0 × 10^{-2}	64.9	3.2	92.3	35.7	2.31	1.59
1.0 × 10^{-3}	38.2	10.1	73.1	96.3	2.65	2.11
1.0 × 10^{-4}	10.8	20.4	83.7	85.6	2.81	1.27
1.0 × 10^{-6}	8.6	0.8	77.3	–	2.89	–
0	7.3	0	–	–	–	–

[a] MMA, 3 cm^3; OC-3, 0.3 g; cellulose, 0.3 g; H_2O, 10 cm^3; 85°C; 3 hr.

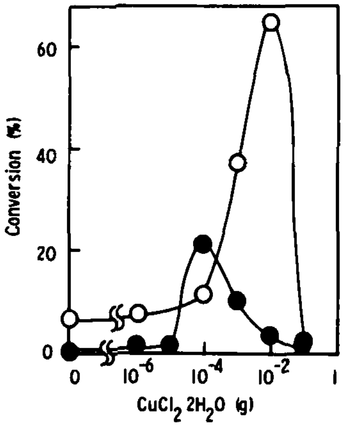
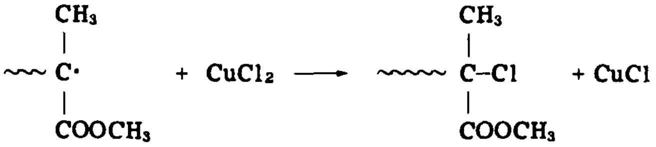


FIG. 2. Conversion of MMA vs. amount of cupric ion: (○) OC-3, 0.3 g; (●) cellulose, 0.3 g; MMA, 3 cm^3; H_2O, 10 cm^3; 85° C; 3 hr.

conversions of MMA were plotted (Fig. 2). It is clearly seen that the presence of cupric ion is necessary for polymerization in the presence of cellulose, while OC-3 could initiate the polymerization of MMA even in the absence of cupric ion. In both cases, cupric ion showed a strong promoting activity for the polymerization. However, with increasing amount of cupric ion, past a given level, cupric ion became an inhibitor, reacting as shown in Eq. (3).



$$\sim\sim\overset{CH_3}{\underset{COOCH_3}{C}}\cdot + CuCl_2 \longrightarrow \sim\sim\sim\overset{CH_3}{\underset{COOCH_3}{C}}-Cl + CuCl \qquad (3)$$

The quantity of cupric chloride which gave a maximum conversion was not the same in the cases of cellulose and oxycellulose. Oxycellulose has more many active points which are able to form a complex with Cu(II) ion than cellulose. For this reason, the maximum quantity of cupric chloride is larger in the case of oxycellulose than in that of cellulose.

It was interesting that $\overline{P}_n$ values of homopoly-MMA obtained with oxycellulose were always larger than those with cellulose, while EG was almost the same in both cases.

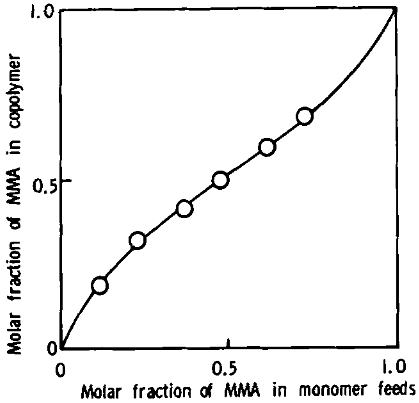


FIG. 3. Copolymerization of MMA and St. OC-3, 0.1 g; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; 85°C; 3 hr.

Proof of Radical Mechanism

Copolymerization of MMA and styrene (St) was carried out under the conditions given in Fig. 3. The composition of the copolymer was determined by elemental analysis, and Fig. 3 was obtained. From this composition curve, the mechanism of the polymerization initiated with the system of oxycellulose, cupric ion and water was concluded to be a radical one.

As another proof for the radical mechanism, the experiments summarized in Table 3 were carried out. Hydroquinone, diphenylpicrylhydrazyl (DPPH), and triphenylverdazyl (TPV) were used as radical scavengers. Addition of these reagents completely inhibited the polymerization.

TABLE 3. Effects of Hydroquinone, DPPH, and TPV on Polymerization[a]

Inhibitor		Conversion
Type	Amt (g)	of MMA (%)
None		13.1
Hydroquinone	0.03	0
DPPH	0.02	0
TPV	0.02	0

[a] MMA, 3 cm^3; OC-3, 0.1 g; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; 85°C; 3 hr.

TABLE 4. Effect of the Amount of Oxycellulose on the Polymerization of MMA[a]

OC-3 (g)	Conversion of MMA (%)	EG (%)	$\overline{P}_n \times 10^{-4}$ homopoly-MMA
0.05	23.0	56.0	2.02
0.10	18.8	50.9	2.02
0.15	18.8	51.5	2.00
0.20	21.0	60.0	2.17
0.25	22.0	62.5	2.06

[a] MMA, 3 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; H_2O, 10 cm^3; 85°C; 4 hr.

Effect of Amount of Oxycellulose on MMA Conversion

The polymerization of MMA was carried out at 85°C for 4 hr with the amounts of MMA, $CuCl_2 \cdot 2H_2O$, and H_2O kept constant at 3 cm^3, 0.01 g, and 10 cm^3, respectively, and with varying amounts of OC-3. The results obtained are summarized in Table 4.

The relationships between the conversion of MMA and the amount of OC-3 after 1, 2, 3, and 4 hr are shown in Fig. 4. After a short

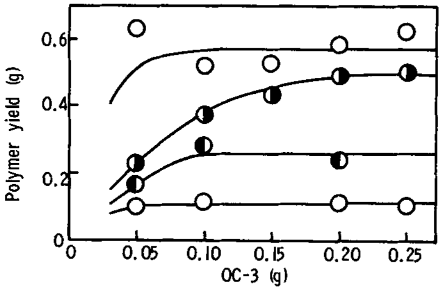


FIG. 4. Polymer yield vs. amount of OC-3 at various polymerization times: (●) 1 hr; (◐) 2 hr; (◑) 3 hr; (○) 4 hr. MMA, 3 cm^3; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; 85°C.

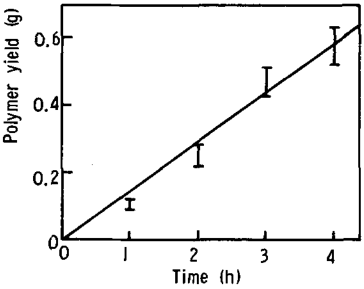


FIG. 5. Polymer yield vs. time.

time, the amount of OC-3 became independent of the conversion. The polymer yields at various polymerization times were plotted against time (Fig. 5). The quantity of polymerized MMA per hour was constant (about 1.4 g under these conditions), regardless of the amount of OC-3 in the feed, probably that the amount of active OC-3 was limited by the action of Cu(II) ion. As mentioned later, the OC-3 molecule, having two CHO groups, forms a complex with Cu(II) ion. By this consideration, 0.01 g of $CuCl_2 \cdot 2H_2O$ corresponds to about 0.01 g of OC-3. Thus, in the experiments in Fig. 4, the large excess of OC-3 was not involved in the main reaction.

Effect of the Amount of MMA on MMA Conversion

The polymerization was also carried out at 85° C for 4 hr with constant amounts of OC-3, $CuCl_2 \cdot 2H_2O$, and H_2O (0.1 g, 0.01 g, and 13 cm^3, respectively) and varying feeds of MMA. The results obtained are summarized in Table 5.

The relation of polymer yields after 1, 2, and 4 hr and the amount of MMA in the feed is shown in Fig. 6. As can be seen, the amount of polymerized MMA was about constant. As in the other cases of uncatalyzed polymerization [11], the polymerization takes place in the aqueous layer. Accordingly, the migration of MMA from the MMA layer into the aqueous phase is the rate-determining step in the polymerization.

TABLE 5. Effect of the Amount of MMA on the Polymerization[a]

MMA (cm^3)	Polymer yield (g)	EG (%)	$\overline{P}_n \times 10^{-4}$ of homopoly-MMA
2	0.451	38.3	2.11
3	0.530	50.9	2.02
4	0.532	50.8	2.40
6	0.688	53.9	2.49

[a] OC-3, 0.1 g; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; H_2O, 13 cm^3; 85°C; 4 hr.

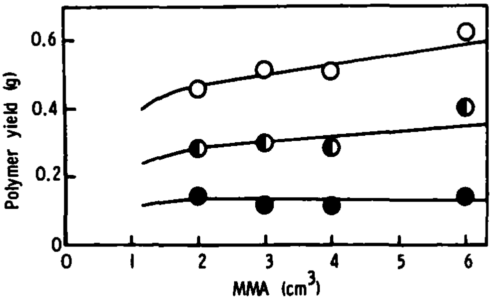


FIG. 6. Polymer yield vs. amount of MMA at various polymerization times: (●) 1 hr; (◐) 2 hr; (○) 4 hr. OC-3, 0.1 g; H_2O, 13 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; 85°C.

Effects of Polymerization Temperature and pH on MMA Conversion

As shown in Fig. 7, a ceiling temperature was seen at about 90°C with OC-3 and OC-4. When the temperature was too high, the formation of complex between Cu(II) ion, oxycellulose, H_2O, and MMA became difficult.

With OC-4 as the oxycellulose, time-conversion curves at 55-85°C (Fig. 8) yielded straight lines. The rates of polymerization R_p were calculated in units of g/hr and put into the Arrhenius relationship. From Fig. 9, the overall activation energy E_a was estimated to be 96.7 kJ/mole.

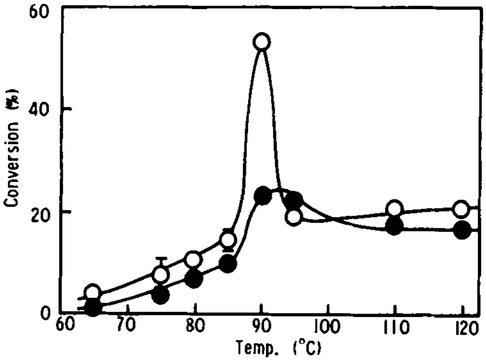


FIG. 7. Conversion vs. temperature: (●) OC-3, 0.1 g; (○) OC-4, 0.1 g. MMA, 3 cm^3; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; 1 hr.

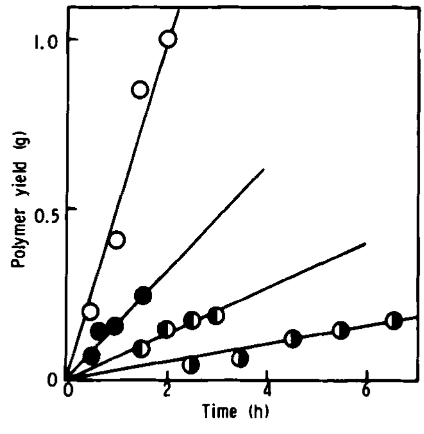


FIG. 8. Polymer yield vs. time with polymerization at various temperatures: (◑) 55°C; (◐) 65°C; (●) 75°C; (○) 85°C. MMA, 3 cm^3; OC-4, 0.1 g; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g.

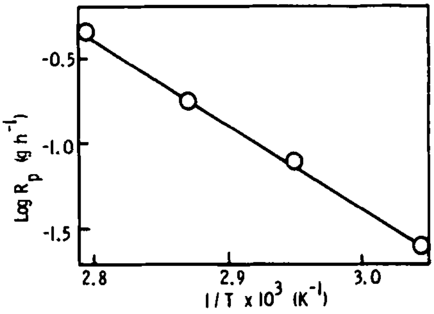


FIG. 9. Arrhenius plot. MMA, 3 cm^3; OC-4, 0.1 g; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g.

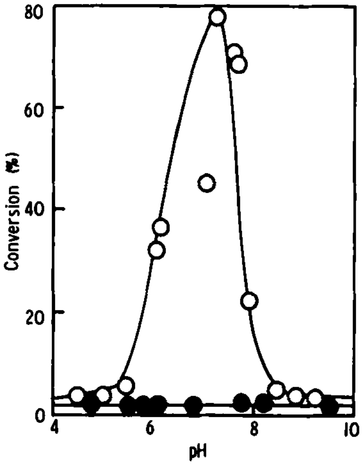
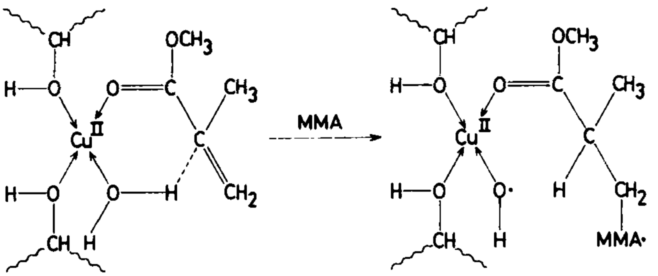


FIG. 10. Conversion vs. pH: (●) OC-4 absent; (○) OC-4 present, 0.1 g. MMA, 3 cm^3; H_2O, 10 cm^3; $CuCl_2 \cdot 2H_2O$, 1.0×10^{-2} g; 85°C; 2 hr. pH 4.3-5.9: M/10 citric acid–M/5 Na_2HPO_4; pH 6.3-8.3: M/20 $Na_2B_4O_7$–M/10 HCl; pH 8.5-9.3: M/15 Na_2HPO_4–M/15 KH_2PO_4.

The pH of the aqueous cupric chloride solution was adjusted by buffer solution, and the conversion plot shown in Fig. 10 was obtained. In a neutral aqueous system, the polymerization took place most easily. The remarkable effect of pH on the conversion cannot be explained at the present time.

Mechanism of Initiation

In 1970, Imoto et al. [12] proposed an initiation mechanism [Eq. (4)]



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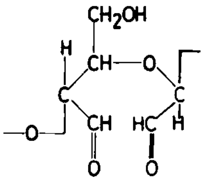
for the polymerization of MMA with the system of cellulose, Cu(II) ion, and water.

Oxycellulose has possible configurations (I-III). The initiation



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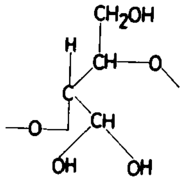

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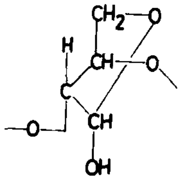
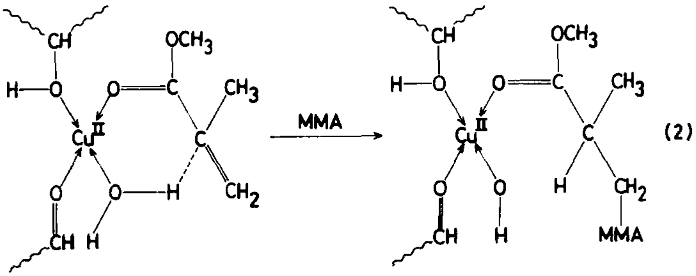


III

mechanism for the system of oxycellulose, Cu(II) ion, and water may be very similar to the case of cellulose; Eq. (5) is therefore proposed for this reaction.



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Accepted by editor May 30, 1976
Received for publication July 22, 1976