A New Choice for the Polymerization Inhibitor in 2-Hydroxyethyl Methacrylate Synthesis

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2-Hydroxyethyl methacrylate (2-HEMA) is one of the most important chemicals produced in large amounts nowadays. It is widely used as a monomer for the production of various resins, varnishes, adhesives, and hydrogels for contact lenses, drug carriers and etc.[1] Generally, it has been synthesized by adding ethylene oxide (EO) to methacrylic acid (MA). The reaction should be carefully controlled by using proper catalysts and inhibitors since the reactants and products can easily be polymerized. So far many catalysts such as tertiary amines,[2] quaternary ammonium salts,[3] metal salts,[4] ion exchange resins,[5] and polymer supported iron catalysts[6] have been reported. As metallic catalysts, Fe(III) salts such as $FeCl_3$, $FeBr_3$, $Fe_2(SO_4)_3$, and $Fe(NO_3)_3$ have been widely used.

Since 2-HEMA contains a vinly group which is vulnerable to the polymerization reaction, inhibitors must be added during the synthesis and purification processes. So far, an extensive search for a more effective synthesis process has been focused on the development of the proper polymerization inhibitors.[7] Among them, some phenol derivatives such as *p*-methoxyphenol (PMP), hydroquinone, and 2,6-di-*t*-butyl-4-methylphenol have been widely used as polymerization retarders, aq. nitrite or nitrate salts have been employed as inorganic inhibitors. But, the inhibition mechanisms for the above mentioned have not been systematically studied so far. We now wish to report some important results about the effect of inhibitors on the 2-HEMA synthesis.

2-HEMA was synthesized from MA and EO by using catalysts such as $FeCl_3 \cdot 6H_2O$, $Na_2Cr_2O_7$, and triethylamine (TEA) (Table 1). The reactions were carried out in an autoclave (Parr model, 4561, SUS 316) at 3.5-5.0 atm. The synthesis procedure was as follows. MA, catalysts and inhibitors were added in an autoclave, followed by a N_2 purge, and the N_2 pressure was adjusted to 2.5-3.0 atm. After the reactor temperature was raised to 85℃, EO was slowly and continuously added for about 30 min. After the completion of the reaction which took about 75-300 minutes, the residual EO was vented out by N_2 stripping, and the products were analyzed by GC[8] and acid-number titration. The results are summarized in Table 1.

As illustrated in the table, when PMP was used as an inhibitor, the reactions were generally sluggish and the polymerization had occurred even with TEA. On the other hand, when aq. $NaNO_3$ was used as an inhibitor, the reactions were fast with high conversion yields.

The inhibition mechanism of PMP is known to be related to the resonance-stabilizing effect of the corresponding phenol radical after losing hydrogen atom to propagating radical. This leads us to postulate that PMP itself can reduce other chemicals, even transition metal complexes. In order to test the validity of this hypothesis, the crude 2-HEMA products were diluted to 1% (v/v) with potassium acetate-acetic acid buffer (1×10^{-2} M, pH 4), then 2 m*l* of 0.01 N aq. phenanthroline solution was added, and the UV-VIS spectra of the resulting solutions were taken. It is known that phenanthroline forms a complex with Fe^{2+} (λ_{max}, 515 nm) and Fe^{3+} (λ_{max}, 394 nm)[9a]. The results showed that the crude product from the PMP system clearly had λ_{max} at 515 nm, while that from the $NaNO_3$ system revealed a shoulder around 354 nm[9b] giving no characteristic of λ_{max} from 370 nm to 515 nm (Figure 1).

Table 1. The Catalytic Activities and the Effects of Inhibitors on 2-HEMA Synthesis[a]

Catalyst[b]	Inhibitor	Reaction time[c] (min)	Conversion[d] of MA
$FeCl_3 \cdot 6H_2O$	$NaNO_3$	160	98%
$Na_2Cr_2O_7$	$NaNO_3$	180	>98.8%
TEA	$NaNO_3$	75	97%
$FeCl_3 \cdot 6H_2O$	PMP	>300	89%
$Na_2Cr_2O_7$	PMP	150	95%
TEA	PMP	180	[e]

[a]Conditions: reaction temperature; 85℃, MA (580 mmol), EO (1.1 eq to MA). Inhibitor; 30% $NaNO_3$ aqueous solution (2.0 mmol), PMP (2.0 mmol). Initial pressure; 3.5 atm under N_2 atmosphere. [b]The amount of catalyst: $FeCl_3 \cdot 6H_2O$ (3.7 mmol), $Na_2Cr_2O_7$ (3.8 mmol), TEA (22 mmol). [c]Determined by the pressure drop to the original one. [d]Determined by acid-number. [e]Polymers were formed.

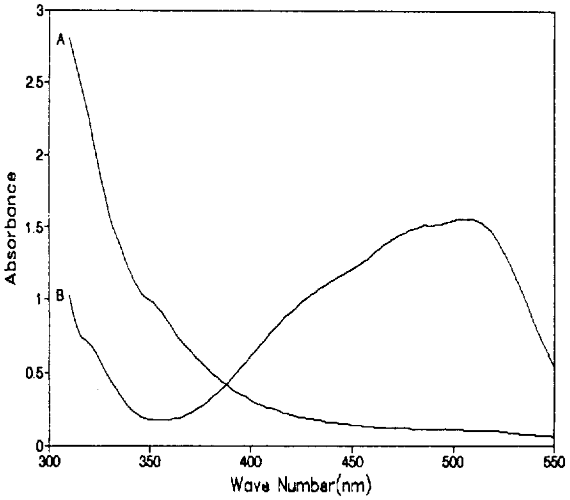

Figure 1. UV-VIS spectrum of iron-phenanthroline complex from A; Crude 2-HEMA products from $FeCl_3 \cdot 6H_2O + NaNO_3$ system, B; Crude 2-HEMA products from $FeCl_3 \cdot 6H_2O$ + PMP system. Condition; 1% (v/v) of crude 2-HEMA in potassium acetate-acetic acid buffer(1×10^{-2} M, pH 4), [Phenanthroline]$=2 \times 10^{-4}$ M.

This implies that Fe^{3+} ion was reduced to Fe^{2+} ion in the PMP system during the course of the reaction. To ascertain the reducing ability of PMP, Fe^{3+} ion in water was reac-

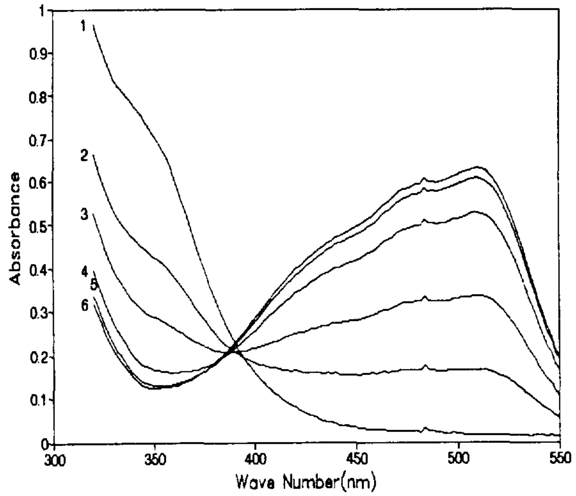

Figure 2. UV-VIS spectra change of iron-phenanthroline complex after addition of PMP to Fe^{3+} ion. Condition; potassium acetate-acetic acid buffer, 1×10^{-2} M, pH 4, 25℃, $[FeCl_3]=3.6\times10^{-4}$, $[PMP]=7.8\times10^{-4}$ M, $[\text{Phenanthroline}]=2\times10^{-4}$ M; after (1) 0 sec, (2) 40 sec, (3) 70 sec, (4) 120 sec, (5) 300 sec, (6) 600 sec.

ted with PMP in a separate experiment, and the products were monitored by taking the UV-VIS spectra as demonstrated in Figure 2. The concentration of $FeCl_3\cdot6H_2O$ was 3.6×10^{-4} M and that of PMP was 7.8×10^{-4} M. Immediately apparent in Figure 2 is that the reduction of Fe^{3+} did occur very quickly, even at room temperature. After 600 seconds, a shoulder an 354 nm was completely disappeared. In the $NaNO_3$ system, however, NO_3^- ion has kept Fe^{3+} ion intact. It could even reoxidize the Fe^{2+} ion to Fe^{3+} ion at 85℃, which was proven by the UV-VIS spectra.[10]

It is desirable in many catalytic reactions to have catalytic systems whose activity is maintained throughout the reaction. Considering the catalytic system utilized in this study, a hard Lewis acid (such as Cr^{6+} and Fe^{3+} ions) seems to have good catalytic activity. This can be accounted for the fact that ethylene oxide, a hard base, can be coordinated to or interact with the hard metal ions for the hydroxyethylation of MA. In the PMP system, PMP reduced Fe^{3+} ion to Fe^{2+} ion, that is, PMP made the catalyst softer, resulting in a loss of the catalytic activity.

The inhibition by $NaNO_3$ may be related to, if any, the formation of O_2 from $NaNO_3$[11] or the oxidizing power of $NaNO_3$. In methacrylic acid medium, $NaNO_3$ could be equilibrated with HNO_3, and with nitrogen dioxide, O_2, and H_2O.[12] The inhibition effect of O_2 had also been reported.[13] Together with the oxidizing power of $NaNO_3$ it can give the maximum inhibition effect in $FeCl_3$ catalyst system. $FeCl_3$ itself has been proved of its high inhibition effect in radical polymerization reaction.[14] Actually, the reduced Fe^{2+} ion formed by any radical can be reoxidized repeatedly by $NaNO_3$.

In conclusion, when amine derivatives or metal catalysts are used in the synthesis of 2-HEMA, $NaNO_3$ which is a mild oxidizing agent is more effective inhibitor than PMP.

References

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8. GC condition was as follows: stationary phase; polyethylene glycol 6000(10%), support; Chromosorb W(AW) DMCS 60-80 mesh, SS, ID; 1/8 inch, length; 2 m. Carrier gas; N_2, injector temperature; 220℃, detector(FID) temperature; 300℃, column temperature; 125℃ (3 min), temperature programming; 2℃/min, final temperature; 150℃ (5 min).
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10. The oxidation condition was as follows: 1×10^{-2} M potassium acetate-acetic acid buffer, pH 4, $[\text{Phenanthroline}]=2\times10^{-4}$ M, $[NaNO_3]=4\times10^{-3}$ M, $[FeCl_2]=2.7\times10^{-4}$ M, 85℃. Even though excess $NaNO_3$ was used, the oxidation reaction of Fe^{2+} ion was not completed. After 30 min, about 10% of Fe^{2+} ion was oxidized to Fe^{3+} ion.
11. O_2 formation was detected by GC. GC condition was as follows: stationary phase; Molecular sieve 5A, SS, ID; 1/8 inch, length; 2 m. Carrier gas; He, injector temperature; 125℃, detector(TCD) temperature; 125℃, column temperature; 110℃. The crude 2-HEMA product (25 ml) from $FeCl_3$ and $NaNO_3$ was added by 1.47 mmol of $NaNO_3$, and cooked at 110℃ in a closed system of 1 atm; The initial area ratio of O_2 to N_2 was 1/200, which was increased to 1/25 after 5 hours.
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