# Free-Radical Polymerization of Methyl Methacrylate Initiated by Thiol Alone

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## SYNOPSIS

Three different alkyl thiols, i.e., $n$-propylthiol, isopropylthiol, and 2-methyl-2-undecanethiol, were proved efficient to initiate the polymerization of methyl methacrylate at 40°C. The initial polymerization rate, $R_p$, increases with increasing thiol concentration but cannot be described by a single-power law. However, $R_p$ is proportional to 1.3th power of the monomer concentration, indicating the participation of monomer in the initiation reaction. With increase of the polarity of solvents, $R_p$ decreases, demonstrating the polar property of the initiating intermediate. The apparent activation energy of overall polymerization was calculated to be 9.3 kcal/mol. Molecular weight measurements indicated the twofold function of the thiol as both an initiator and a regulator.

## INTRODUCTION

It is well known that thiol is a molecular weight regulator for a free-radical chain polymerization. Thiol acid as a component of redox system was also reported to promote the polymerization of acrylate monomers.[1] Recently, it has been proved that thiol can initiate the copolymerization of CTC (charge transfer complex) type comonomers such as styrene–acrylonitrile[2] and styrene–$N$-phenylmaleimide.[3] However, thiol does not initiate the homopolymerization of either monomers of the CTC. Methyl methacrylate (MMA) is the first example of homopolymerization that is initiated by thiol alone. In this work different thiols were used to show the structural effect of the thiol on initiation reactivity. The variation of initial polymerization rate with thiol concentration and monomer concentration was investigated separately in order to examine whether MMA is involved in initiation or not. The effect of the polarity of the solvent on polymerization rate was studied as well to reveal the nature of the initiating species. Molecular weight measurements

show that thiol acts as both initiator and chain transfer agent in the polymerization.

## EXPERIMENTAL

### Materials

MMA, polymerization grade, dried with calcium hydride, was distilled at reduced pressure immediately before use. Thiols (RSH) are commercial products of Fluka AG. Solvents were dried and distilled before use.

### Polymerization

Polymerization kinetic studies were performed in dilatometers. Prior to polymerization, the dilatometer filled with reactants was repeatedly degassed and finally sealed under vacuum so that the reaction system is free of oxygen. Monomer conversion was controlled at less than 5%. The initial polymerization rate is given by the following expression (in mol/l s):

$$R_p = \frac{\Delta V \times 1000}{M_0 V_0 (1/d_0 - 1/d_p)}$$

where $M_0$ is the molecular weight of the monomer unit in the polymer, $1/d_p$ is the specific volume of the polymer, $1/d_0$ is the specific volume of monomer, $\Delta V$ (in mL/s) is the contraction rate of the reactant volume, and $V_0$ is the initial reactant volume. Molecular weight was determined by gel permeation chromatography (GPC) with polystyrene as standard.

## RESULTS AND DISCUSSION

### General

In this work it was found for the first time that alkyl thiols can initiate the polymerization of MMA at 40°C or lower temperature, with an induction period of less than 30 min. Three different thiols were used for a comparison of their reactivities. Figure 1 shows that the reactivity order is as follows:

isopropyl-SH < 2-methyl-2-undecane-SH

< n-propyl-SH
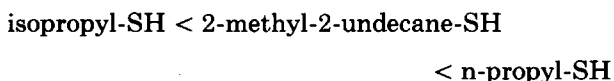
which is not in agreement with the magnitude order of their chain transfer constants, which is[4]

$$RCH_2SH > RR'CHSH > RR'R''CSH$$

This indicates that the mechanism of the initiation here is different from that of chain transfer.



**Figure 2** Plot of initial polymerization rate $R_p$ vs. [RSH], [M] = 5.55 mol/L, $T$ = 40°C; solvent: methyl ethyl ketone.

### Specific

In the following investigation, only 2-methyl-2-undecanethiol was used. The effect of the concentration of RSH on initial polymerization rate, $R_p$, was examined over a wide concentration range. As shown in Figure 2, $R_p$ increases with the increasing of RSH concentration but cannot be described by a single-power law. The upward trend of the curve of $R_p$ versus [RSH] is greatly reduced at high concentrations of RSH, which can be ascribed to the consumption of RSH in a fast chain transfer reaction. Similar



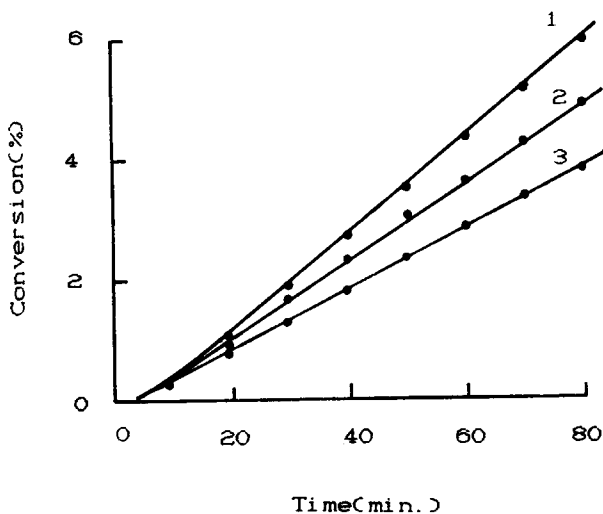**Figure 1** Monomer conversion vs. reaction time, [M] = 5.55 mol/L, [RSH] = 1.37 × $10^{-2}$ mol/L; solvent: methyl ethyl ketone, $T$ = 40°C; (1) isopropylthiol; (2) 2-methyl-2-undecane-thiol; (3) $n$-propylthiol.



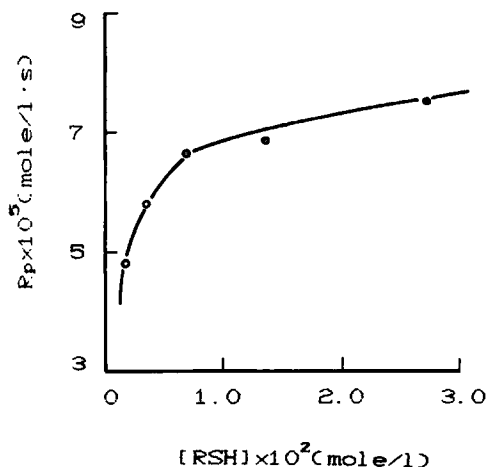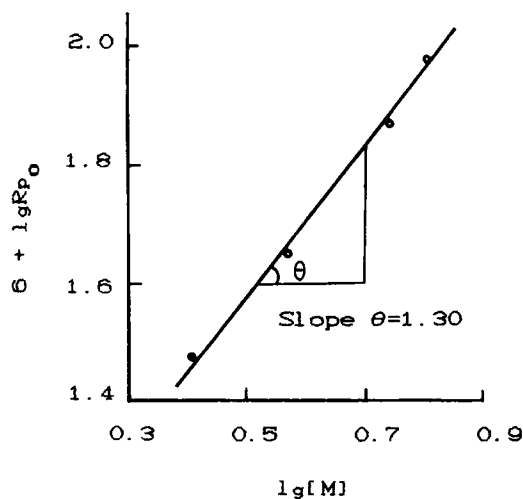**Figure 3** Relationship between initial polymerization rate $R_p$ and monomer concentration [M], [RSH] = 1.37 × $10^{-2}$ mol/L, $T$ = 40°C; solvent: methyl ethyl ketone.

**Table I  Effect of Solvent on Polymerization Rate[a]**

| Solvent | Dielectric Constant[5] | $R_p \times 10^5$ mol/L s |
|---|---|---|
| Toluene | 2.3 | 7.59 |
| Tetrahydrofuran | 7.2 | 6.81 |
| Methyl ethyl ketone | 18.5 | 6.09 |

[a] [M] = 5.55 mol/L, [RSH] = $1.37 \times 10^{-2}$ mol/L, $T$ = 40°C.

results have been observed in redox polymerization involving thiols.[1]

At monomer concentration [M] ranging from 2.0 to 7.0 mol/L, the relationship between initial polymerization rate and monomer concentration was studied carefully. It was found from Figure 3 that the slope of the plot of lg $R_p$ vs. lg[M] is 1.30, i.e., $R_p \propto$ [M]$^{1.30}$. This experimental result indicates that the monomer participates in the initiation reaction. The involvement of monomer in initiation is a characteristic of the thiol-initiated polymerization.

The studies on polymerization kinetics were carried out in different solvents to examine the effect of reaction media. The initial polymerization rate, $R_p$, together with the dielectric constants of solvents are listed in Table I. It is evident that the variation of $R_p$ with solvent is related to the polarity of the solvents. Generally, the propagating radical species is not very solvent-dependent unless some unusual conditions are operative.[6] Therefore, the solvent effect observed here may be attributed to the influence of the polarity of solvent on the initiation reaction producing a primary free radical. A solvent affects the overall polymerization by affecting the initiation process.

The temperature dependence of $R_p$ was measured from 35 to 45°C. The plot of ln $R_p$ vs. $1/T$ is shown in Figure 4, and the apparent activation energy, $E_a$, was calculated to be 9.3 kcal/mol. The earlier reported values of $E_a$ for the polymerization of MMA
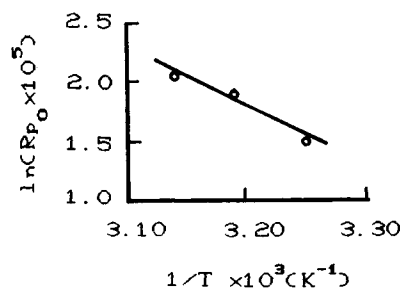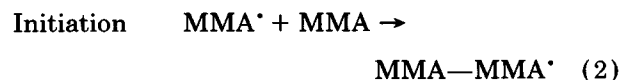


**Figure 4**  Plot of ln $R_p$ vs. $1/T$, [M] = 5.55 mol/L, [RSH] = $1.37 \times 10^{-2}$ mol/L; solvent: methyl ethyl ketone.

initiated by redox systems are ranged from 8.3 to 8.9 kcal/mol.[1]

The variations of molecular weight with [RSH] are listed in Table II. According to free-radical polymerization theory, the inverse of number-average molecular weight, $1/M_n$, should be proportional to the concentration of the regulator.[7] A deviation is noted here from that predicted by the classical theory, and molecular weight decreases slightly with the increasing of [RSH]. A reason for this phenomenon is that RSH mainly plays a role of initiator in present case.

The initiation may be as follows:

Hydrogen transfer     RSH + MMA →

$$RS^{\bullet} + MMA^{\bullet} \quad (1)$$

Initiation     MMA$^{\bullet}$ + MMA →

$$MMA—MMA^{\bullet} \quad (2)$$

$$RS^{\bullet} + MMA \rightarrow RS—MMA^{\bullet} \quad (3)$$

The rate-determining step is reaction (1). The intermediate producing a primary radical will be a polar one since it is influenced by the polarity of solvent as mentioned earlier. The involvement of MMA in hydrogen transfer process is indirectly confirmed by the kinetic expression of $R_p \propto$ [M]$^{1.30}$. The incorporation of RS group into polymer chain has been verified by using $^1$H-NMR spectra.[3]

**Table II  Relationship between Molecular Weight and [RSH]**

| [RSH] × $10^2$ (mol/L) | $M_n \times 10^{-4}$ | $1/M_n \times 10^6$ | $M_w \times 10^{-4}$ | $M_w/M_n$ |
|---|---|---|---|---|
| 0.34 | 22.8 | 4.39 | 44.4 | 1.95 |
| 0.68 | 15.2 | 6.58 | 30.4 | 2.00 |
| 1.37 | 11.8 | 8.48 | 22.6 | 1.92 |
| 2.74 | 9.22 | 10.9 | 16.9 | 1.83 |

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