

SHORT COMMUNICATIONS

**Polymerization of Methyl Methacrylate Initiated
by Benzenesulfonic Acid**

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Hagger observed that methyl methacrylate (MMA) polymerizes in the presence of toluenesulfonic acid.¹ A certain number of studies have been reported on the polymerization of vinyl monomers using sulfonic acids,²⁻⁷ in which sulfonic acids act as reductants to generate radical species in the redox systems containing oxidants. Some sulfonic acids are used with photosensitizers for photo-induced radical polymerizations.⁸⁻¹⁰

Overberger *et al.*¹¹ have investigated the polymerization of MMA initiated by benzenesulfonic acid alone and assumed that radical species formed by the reaction of the sulfonic acid initiated the polymerization. However, the detailed mechanism of the polymerization is obscure, because hydroquinone does not inhibit but accelerate the polymerization and the rate is first order with respect to the concentration of benzenesulfonic acid, whereas Hagger reported the rate to be proportional to the square root of the concentration of toluenesulfonic acid, in which small amounts of oxygen might act as oxidant to initiate redox radical polymerization.¹

Thiols initiate the radical polymerization of vinyl monomers in redox systems containing oxidants. We reported that some monomers with α,β -unsaturated carbonyl groups, such as MMA and *N*-substituted maleimides, are

polymerized by thiophenol without any oxidant.^{12,13} A plausible mechanism for this polymerization comprises an ionic process, in which both initiation and propagation take place *via* reactions similar to the Michael addition. Since sulfonic acids add to α,β -unsaturated carbonyl compounds similarly,¹⁴⁻¹⁶ the polymerization initiated by a sulfonic acid alone seems to proceed *via* such a process.

This paper discusses the mechanism of polymerization of MMA initiated by benzenesulfonic acid on the basis of ionic reactions.

EXPERIMENTAL

Materials

Benzenesulfonic acid was obtained as prisms by acidifying an aqueous solution of sodium benzenesulfinate (10 g/40 ml) with conc. hydrochloric acid (4.1 ml). The crystalline acid was separated by filtration and dried *in vacuo* over phosphorous pentoxide, 4.9 g (yield 69%), mp 73.5—75°C (lit.¹⁴ 74—76°C); the acid was stored under nitrogen at 5°C. MMA was purified by distillation according to the conventional method. Other special grade reagents and solvents were used without further purification.

Polymerization

A given amount of benzenesulfonic acid was taken in a glass tube, and flushed with argon. MMA was added and the tube was stoppered with a rubber septum and cooled in an ice bath. After argon was bubbled through the solution for 10 min using injection needles, the tube was placed in a bath thermostated at 30°C to start the polymerization. At certain time intervals, the tube was taken out from the bath and contents poured into methanol to precipitate the polymer. The conversion was gravimetrically determined.

GPC Measurements

Gel permeation chromatography (GPC) was performed with a JASCO PU-980 HPLC pump system equipped with a Shodex GPC column (KD-80 M), using DMF containing lithium bromide (0.01 M) as the eluent. Number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w) of the polymers were calibrated with standard polystyrenes.

RESULTS AND DISCUSSION

The results of the polymerization of MMA initiated by benzenesulfonic acid are shown in Figure 1. The polymerization took place in the presence of a sulfonic acid without an oxidant,

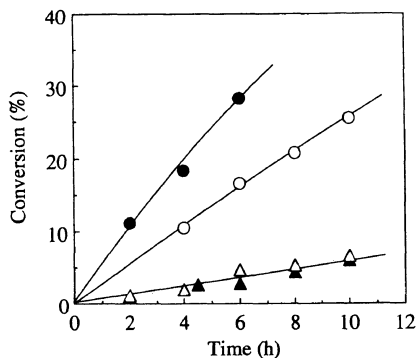


Figure 1. Effects of hydroquinone on the polymerization of MMA initiated by benzenesulfonic acid. MMA, 18.8 mmol; BSA, 0.4 mmol; (○) bulk, hydroquinone nil; (●) bulk, hydroquinone 0.8 mmol; (△) DMF, 2 ml, hydroquinone nil; (▲) DMF, 2 ml, hydroquinone 0.8 mmol.

and hydroquinone as an inhibitor for radical chain reactions did not inhibit but somewhat accelerated the bulk polymerization. The solution polymerization in *N,N*-dimethylformamide (DMF) proceeded at a relatively small rate, which in the presence of hydroquinone was almost the same as that in its absence, indicating polymerization to proceed by a non-radical mechanism.

We previously reported a polymerization of MMA initiated by thiophenol where polymerization proceeds *via* an ionic process including a zwitterionic intermediate.¹² In that case, no polymer was formed in highly polar dimethyl sulfoxide (DMSO), and trace amounts of polymer were obtained in DMF. Inhibition of polymerization in such highly polar solvents is explained as follows: the enhanced rate of termination surpasses the rate of propagation, where only an adduct of thiophenol to the monomer and/or telomers are formed.

Polymerization with benzenesulfonic acids, however, gave polymers with high molecular weights even in DMF or DMSO as shown below, though conversion was low. Although 1,1-diphenyl-2-picrylhydrazyl (DPPH) is an effective radical scavenger, as Figure 2 shows, no induction period was observed in the presence of this inhibitor. This also is indicative of a non-radical mechanism. Although DPPH

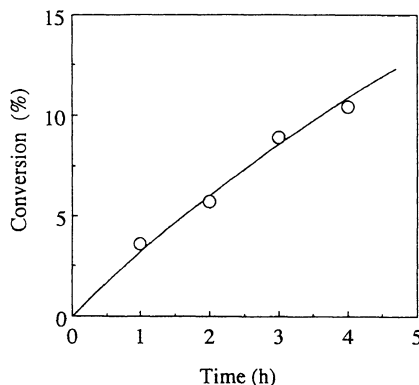


Figure 2. Polymerization of MMA with benzenesulfonic acid in the presence of DPPH. MMA, 9.4 mmol; BSA, 0.2 mmol; DPPH, 0.2 mmol.

Table I. Effects of DPPH^a

| DPPH mmol | Conversion % | \bar{M}_n^b $\times 10^{-3}$ | \bar{M}_w/\bar{M}_n |
|--------------|-----------------|-----------------------------------|-----------------------|
| 0 | 25.6 | 299 | 1.51 |
| 0.1 | 31.1 | 93 | 1.62 |
| 0.2 | 33.6 | 66 | 1.49 |
| 0.4 | 31.8 | 62 | 1.37 |
| 0.8 | 28.8 | 47 | 1.27 |

^a MMA 18.8 mmol, BSA 0.4 mmol, 10 h. ^b DMF containing LiBr (0.01 M) was used as the eluent for GPC measurement.

Table II. Effects of solvent on the polymerization of MMA^a

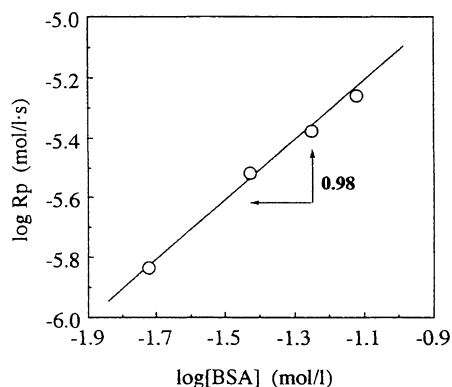
| Solvent | Conversion/% | $\bar{M}_n/\times 10^{-3}$ | \bar{M}_w/\bar{M}_n |
|--------------|--------------|----------------------------|-----------------------|
| Benzene | 20.4 | 199 | 1.70 |
| Acetonitrile | 12.1 | 181 | 1.62 |
| DMF | 6.6 | 1680 | 2.26 |
| DMSO | 2.8 | >2000 ^b | 2.16 |

^a MMA, 18.8 mmol; BSA, 0.4 mmol; solvent, 2 ml, 10 h.

^b Exclusion limit of the column was 2×10^6 .

did not inhibit the polymerization, its effect on the molecular weight of the polymer should be noted (Table I). The addition of DPPH (0.1 mmol) caused great decrease in \bar{M}_n and small increase in the rate of polymerization. The molecular weight distribution narrowed with increasing concentration of DPPH. \bar{M}_w/\bar{M}_n of 1.27 with DPPH (0.8 mmol) is rather small compared to that obtained in radical polymerization. Usually, decrease in \bar{M}_n arises from decrease in the rate of propagation, increase in the rate of termination, and/or increase in the rate of chain transfer. In each case, the rate of polymerization decreases. In this case, addition of the radical scavenger caused small increase in the rate and marked decrease in \bar{M}_n . The effects of DPPH on the polymerization kinetics are obscure.

The solvent effect on polymerization was subsequently examined. Table II shows that conversion decreased in polar solvents, while \bar{M}_n increased remarkably in DMF and DMSO,

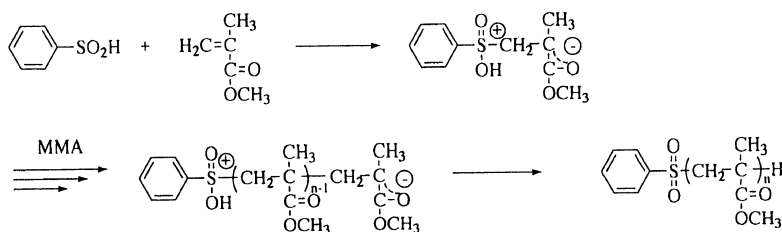

Figure 3. Dependence of the rate of polymerization on BSA concentration. MMA, 9.4 mmol; benzene, 4 ml.

and MWD widened slightly.

In usual radical polymerizations, decrease in the concentration of the initiator results in decrease of the rate and increase in \bar{M}_n . On the basis of experimental results, the present polymerization is supposed to proceed *via* a non-radical process. Ionic reactions are expected to be relatively fast in polar solvents. Since this polymerization is assumed to be an ionic chain reaction, all initiation, propagation, and termination reactions should be affected by solvent polarity. The rate of polymerization and molecular weight of the polymer result from a combination of these reactions. Consequently, this marked change in the conversion and \bar{M}_n in the polar solvents is suggestive of an ionic mechanism for the polymerization.

The polymerization rate was first order with respect to the concentration of benzenesulfinic acid (Figure 3). This also indicates that the polymerization is initiated by a non-radical reaction.¹⁷

The polymerization of styrene with this sulfinic acid was extremely slow. The conversion in DMF at 30°C was less than 2% after 2 days. As we reported previously, styrene was not polymerized by thiophenol and copolymerization of MMA with styrene did not proceed.¹² Copolymerization initiated by benzenesulfinic acid also did not occur. These re-



Scheme 1.

sults suggest that polymerization with benzenesulfonic acid takes place *via* a process similar to that with thiophenol.

ESR measurements using 2-methyl-2-nitrosopropane and nitrosodurene as spin trapping reagents revealed the absence of radical species under the polymerization conditions. This also indicates that the polymerization is non-radical. The nucleophilic addition of benzenesulfonic acid to aryl acrylates has been reported,¹⁵ in which the reaction takes place in a manner similar to the Michael addition as thiophenol adds to α,β -unsaturated carbonyl compounds. Observations on polymerizations with these sulfur compounds are similar. For example, the formation of poly-MMA was difficult in much polar solvents. Accordingly, polymerization with benzenesulfonic acid may take place *via* a mechanism similar to that reported previously for polymerization with thiophenol.¹² The configurational syndiotactic-rich structure of poly-MMA obtained was very similar to those polymers formed with thiophenol or ordinary radical initiators. The reason why no copolymer of MMA with styrene was obtained can be explained by the rapid addition of protons to the unstable anionic chain end of styrene. That is, propagation is instantaneously terminated by the protonation forming the Michael adduct.

In the polymerization of MMA with thiophenol, increased amounts of initiator up to 100% to the monomer resulted in only the Michael adduct and telomers.¹² In the case of benzenesulfonic acid, polymers with high molecular weights were obtained even in the

Table III. Benzenesulfonic acid-initiated polymerization of MMA^a

| BSA/mol% | Conversion/% | $\bar{M}_n (\times 10^{-3})$ | \bar{M}_w/\bar{M}_n |
|----------|--------------|------------------------------|-----------------------|
| 20 | 13.1 | 1582 | 2.31 |
| 50 | 15.6 | 902 | 1.92 |
| 100 | 24.6 | 361 | 1.74 |
| 200 | 37.1 | 174 | 1.58 |

^a MMA, 1.88 mmol; DMSO, 2 ml, 24 h.

presence of 200 mol% of the initiator, as shown in Table III. Reactions of aryl sulfonic acids with aryl acrylates gave the Michael adducts in high yields,¹⁵ because, after the nucleophilic addition of the sulfur of the acid to the β -carbon of the vinyl group, protonation was faster than the propagation by the addition of the anionic end to additional monomers. In the case of MMA, propagation seemed to proceed to a certain extent before termination by protons.

Polymerization reflects a balance between propagation and termination reactions. We are investigating the polymerization of other α,β -unsaturated carbonyl monomers using sulfonic acids and have recently found that *N*-substituted maleimides and acrylamide derivatives are polymerized by benzenesulfonic acid.¹⁸ The polymerization of acrylic acid in water is likely to proceed partially through radical reactions because the inhibitory effect of hydroquinone was observed. Further investigation to elucidate the detailed mechanism is in progress.

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