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RADICAL POLYMERIZATION OF VINYL MONOMERS IN THE PRESENCE OF ETHYL α-BENZENE- AND α-*p*-TOLUENESULFONYLMETHYLACRYLATES

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Abstract—Ethyl α-benzene-(EBSA) and α-toluenesulfonylmethylacrylate (ETSA) were found to show no homopolymerizability but to act as effective chain transfer reagents in radical polymerizations of methyl methacrylate (MMA), styrene (St) and *n*-butyl acrylate (BA), being conjugative monomers. The estimated chain transfer constants (C_T) are as follows; C_t(EBSA) = 0.73(50°C) and 0.72(60°C) for MMA, 4.80(50°C) and 4.21(60°C) for St, 1.78(50°C) and 1.69(60°C) for BA; C_T(ETSA) = 1.09(60°C) for MMA, 6.80(60°C) for St, 2.31(60°C) for BA. i.r. and ^{1}H-NMR spectra of poly(MMA) and poly(St) formed in the presence of EBSA and ETSA are consistent with the view that the polymers bear a C═C bond at one terminal and an arenesulfonyl group at the other. These findings indicate that the ethyl α-arenesulfonylmethylacrylates undergo chain transfer reaction via an addition-fragmentation mechanism.

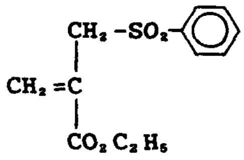
INTRODUCTION

It is well known that α, α-disubstituted monomers are not easily polymerized by radical initiators. In fact, α-methylstyrene and ethyl α-*n*-butylacrylate yield no polymers by conventional radical polymerization because of steric hindrance due to their substituents [1].

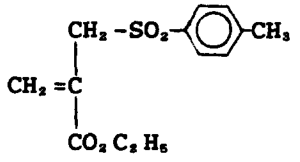
On the other hand, dialkyl itaconates (DRI) and alkyl α-acyloxymethylacrylates (RAA) are readily polymerized by radical initiators in spite of their bulky α-substituents [2–7]. Furthermore, interestingly, the polymerizations of these monomers involve ESR-observable propagating polymer radicals under the actual polymerization conditions. It is also noteworthy that RAA has much a higher rate constant of propagation than DRI although they have similar structures [6, 7].

During our study on the polymerization of α, α-disubstituted monomers, recently we have examined the behaviors of ethyl α-benzenesulfonylmethylacrylate (EBSA) and α-*p*-toluenesulfonylmethylacrylate (ETSA) in radical polymerization. It has been found that EBSA and ETSA show no homopolymerizability under the usual conditions for radical polymerization but they act rather as effective chain transfer reagents by an addition-fragmentation mechanism. The addition-fragmentation chain transfer mechanism was proposed by Meijs and Rizzard [8, 9]. EBSA was only mentioned as such a transfer reagent [10]. Unlike mercaptans and disulfides widely used as chain transfer reagents, EBSA and ETSA do not have objectionable odors.

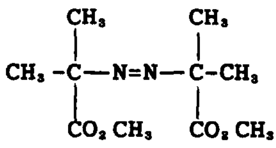
The present paper deals with kinetic and ESR results on the effects of EBSA and ETSA on the radical polymerizations of vinyl monomers with dimethyl 2,2′-azobisisobutyrate (MAIB) as initiator.



(EBSA)



(ETSA)



$$\mathrm{CH_3{-}C(CH_3)(CO_2CH_3){-}N{=}N{-}C(CH_3)(CO_2CH_3){-}CH_3}$$

(MAIB)

EXPERIMENTAL PROCEDURES

Materials

EBSA was prepared thus. Ethyl α-hydroxymethylacrylate (EHMA) was obtained by the reaction of triethylphosphonoacetate with formaldehyde in the presence of potassium

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carbonate according to the method of Villeras *et al.* [11]. EHMA was converted to ethyl α-bromomethylacrylate (HBMA) by treating with PBr_3. The reaction mixture consisted of acetone (150 ml), EBMA (19.3 g), sodium benzenesulfinate dihydrate (22.0 g), and tetra-*n*-butylammonium bromide (TBA) (0.2 g) as a phase transfer catalyst and was stirred for 2.5 hr at room temperature. The resulting sodium bromide and unreacted sodium benzenesulfinate were filtered off, and evaporation was carried out at room temperature. Benzene was added to the residue. The precipitated TBA was filtered, and the filtrate was evaporated. Double distillation of the residue gave pure EBSA; yield: 60%, b.p. 170/1 mm Hg.

i.r. (neat) (cm^{-1}): 1713(—COO—); 1630(—C=C—); 1600(-phenyl); 1149, 1307(—SO_2—). ^{1}H-NMR($CDCl_3$) (TMS, ppm): 1.2(t; —O—CH_2—CH_3, 3H); 4.0(q; —O—CH_2—CH_3, 2H); 4.2(s; —C=C—CH_2—SO_2—, 2H); 5.9, 6.5(CH_2=C—, 2H); 7.1–8.0(—C_6H_5, 5H).

Elemental analysis. $C_{12}H_{14}O_4S$(254.3): calculated C 56.68, H 5.55; found C 56.74, H 5.44.

ETSA was similarly prepared by the reaction of EBMA with sodium *p*-toluenesulfinate tetrahydrate in acetone at room temperature in the presence of TBA as phase transfer catalyst. Crude ETSA was twice recrystallized from a toluene–hexane mixture; yield: 80%, m.p. 46°C.

i.r. (KBr)(cm^{-1}): 1717(—COO—); 1628(—C=C—); 1600(-phenyl); 1315, 1136(—SO_2—). ^{1}H-NMR($CDCl_3$) (TMS, ppm): 1.2(t; —O—CH_2—CH_3, 3H); 2.4(s; —C_6H_4—CH_3, 3H); 4.0(q; —O—CH_2—CH_3, 2H); 4.1(s; —C=C—CH_2—SO_2—, 2H); 5,8, 6.4(CH_2=C—, 2H); 7.1–7.9(—C_6H_4—CH_3, 4H).

Elemental analysis. $C_{13}H_{16}O_4S$(268.3): calculated C 58.19, H 6.01; found C 57.92, H 5.92.

Commercial styrene (St), methyl methacrylate (MMA), *n*-butyl acrylate (BA) and vinyl acetate (VAc) were freed of inhibitor by treating with a 5% NaOH aqueous solution and distilled. Benzene was purified by the usual method. MAIB (Wako Pure Chemical Industries) was recrystallized from methanol.

Polymerization

Polymerizations were performed in degassed and sealed tubes. Polymers were isolated by pouring the polymerization mixture into a large amount of methanol or n-hexane, filtered, dried in vacuum, and weighed.

Measurements

Gel permeation chromatograms (GPC) were recorded at 38°C, using a Toso-HLC 802A instrument with tetrahydrofuran as eluent. From GPC results, the number-average ($\bar{M}_n$) and wight-average ($\bar{M}_w$) molecular weights of the polymers were determined using polystyrene standards. ^{1}H-NMR spectra of EBSA, ETSA and the resulting polymers were obtained in $CDCl_3$ using Hitachi R-24B (60 MHz) and JEOL EX-400 (400 MHz) spectrometers. ESR spectra of the polymerization mixtures were recorded with a JEOL-JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity. Dynamic thermogravimetry (TG) of the polymers was studied in N_2 (flow rate 20 ml/min) with a Shimadzu TGA-50 thermogravimeter at a heating rate of 10°C/min. All runs were terminated at 500°C.

RESULTS AND DISCUSSION

Attempted polymerization of EBSA and ETSA by radical initiation

In order to examine the homopolymerizability of α-arenesulfonylmethylacrylates, polymerizations of EBSA (1.0 mol/l) and ETSA (0.75 mol/l) with MAIB (5.0×10^{-2} mol/l) were attempted in acetone for 6 and 12 hr, respectively. However, no polymers were formed, as confirmed by GPC curves of the polymerization mixtures. This behavior of α-arenesulfonylmethylacryates is distinct from those of DRI and RAA.

Table 1. Polymerization of MMA with MAIB for 1.5 hr at 50°C in benzene in the presence of EBSA*

10^2 [EBSA] (mol/l)	Conversion (%)	$\bar{M}_n/10^3$
0	13.1	71.2
1.00	13.3	30.6
2.00	11.7	19.8
3.00	13.9	13.9
4.00	12.4	10.8
5.00	11.8	9.0

*[MMA] = 3.76 mol/l; [MAIB] = 5.00×10^{-2} mol/l.

Next, we investigated the behaviors of EBSA and ETSA as chain transfer agents in radical polymerization.

Polymerization of MMA with MAIB in benzene in the presence of EBSA and ETSA

Table 1 summarizes the results of polymerization of MMA with MAIB at 50°C in benzene in the presence of EBSA. The presence of EBSA caused a marked decrease in the molecular weight of the resulting poly(MMA), but exerted little effect on the polymer yield. These findings indicate that EBSA is an effective chain transfer reagent for the radical polymerization of MMA.

Chain transfer constant (C_T) was estimated by the plot in Fig. 1 according to the Mayo equation (1).

$$1/\overline{DP}_n = 1/\overline{DP}_{n0} + C_T\{[\mathrm{EBSA}]/[\mathrm{MMA}]\} \qquad (1)$$

where $\overline{DP}_{n0}$ and $\overline{DP}_n$ are the number-average degrees of polymerization in the absence and presence of EBSA, respectively. C_T values thus obtained are 0.73 at 50°C and 0.72 at 60°C.

C_T of ETSA in the polymerization of MMA was estimated similarly and found to be 1.09 at 60°C.

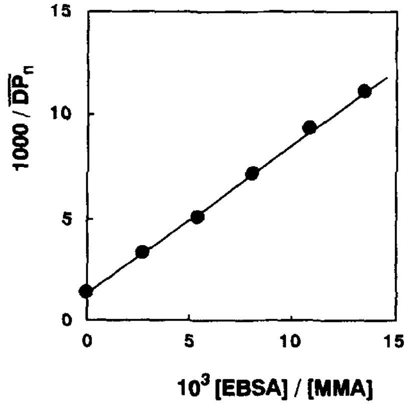


Fig. 1. The Mayo plot for the polymerization of MMA in benzene with MAIB in the presence of EBSA at 50°C; [MMA] = 3.76 mol/l, and [MAIB] = 5.0×10^{-2} mol/l.

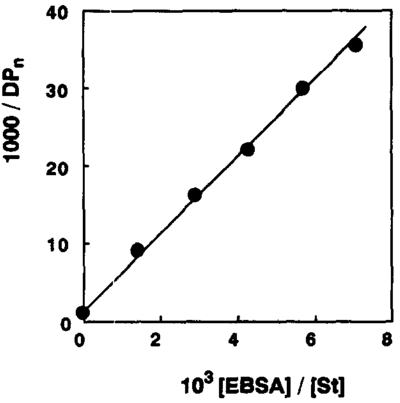


Fig. 2. The Mayo plot for the polymerization of St in benzene with MAIB in the presence of EBSA at 50°C; [St] = 3.46 mol/l, and [MAIB] = 1.0×10^{-2} mol/l.

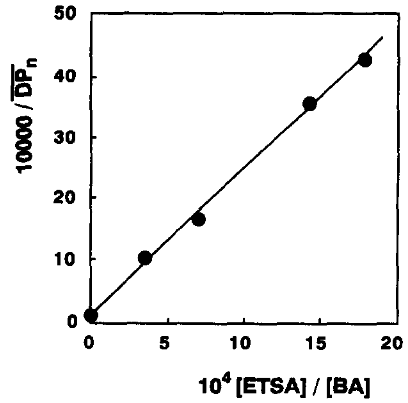


Fig. 3. The Mayo plot for the polymerization of BA in benzene with MAIB in the presence of ETSA at 60°C; [BA] = 3.46 mol/l, and [MAIB] = 1.0×10^{-2} mol/l.

Polymerization of St with MAIB in benzene in the presence of EBSA and ETSA

EBSA and ETSA were found to be effective transfer reagents for the St polymerization. Figure 2 shows the Mayo plot for polymerization in the presence of EBSA at 50°C. From the slopes of such plots, the C_T values of EBSA and ETSA were found as follows; C_T (EBSA) = 4.80(50°C), 4.21(60°C) and C_T (ETSA) = 6.80(60°C).

Polymerization of BA with MAIB in benzene in the presence of EBSA and ETSA

The effects of EBSA and ETSA on the polymerization of BA with MAIB in benzene were also examined. As for the cases of MMA and St, the presence of EBSA or ETSA caused a pronounced decrease in the molecular weight of resulting polymer, but had little effect on the polymer yield.

Figure 3 shows the Mayo plot for polymerization of BA in the presence of ETSA at 60°C. The slope of this plot gave a C_T of 2.31. Similarly the C_T value of EBSA was determined to be 1.78 at 50°C and 1.69 at 60°C.

Polymerization of VAc with MAIB in benzene in the presence of EBSA

Table 2 summarizes the results of polymerization of VAc in the presence of EBSA at 50°C. When EBSA was added to the polymerization system, not only the molecular weight of poly(VAc) but also the polymer yield was decreased. Thus EBSA acted as a retarder in the polymerization of VAc.

Table 2. Polymerization of VAc with MAIB in benzene for 8 hr at 50°C in the presence of EBSA*

10^3 [EBSA] (mol/l)	Conversion (%)	$\bar{M}_n/10^4$
0	14.2	15.9
1.00	11.7	11.7
2.00	9.5	9.2
3.00	9.0	7.7
4.00	7.4	6.4
5.00	6.2	5.4

*[VAc] = 4.30 mol/l;
[MAIB] = 5.00×10^{-3} mol/l.

Polymerization mechanism of vinyl monomers in the presence of α-arenesulfonylmethylacrylate ester

As mentioned above, EBSA and ETSA were found to act as effective chain transfer reagents in the radical polymerizations of conjugative vinyl monomers.

In order to elucidate the chain transfer mechanism for the ethyl α-arenesulfonylmethylacrylates, we have examined the polymerization systems by means of ESR.

Figure 4 shows the ESR spectra observed for the MMA/MAIB/EBSA/benzene system under photoirradiation where a 500 W Xe-lamp was used as light source. The observed five-line spectrum is closely similar to those of the propagating polymer radicals of itaconic acid esters and related monomers [2–5, 12], and is assignable to polymer radical II generated in the following chain transfer reaction via

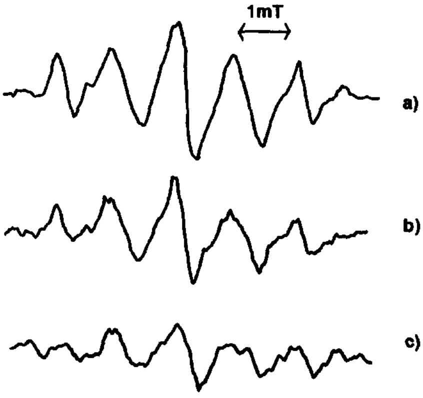
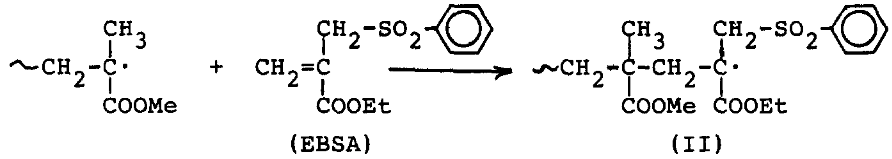
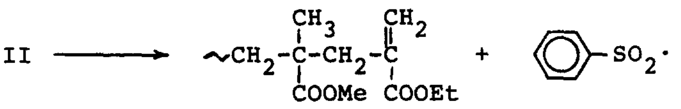


Fig. 4. ESR spectra of MMA/MAIB/EBSA/benzene system under photoirradiation; (a) at 20°C, (b) at 40°C and (c) at 70°C.

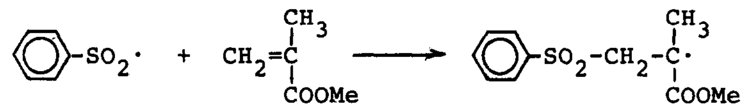
an addition-fragmentation mechanism:



(2)



(3)



(4)

As can be seen from the figure, the intensity of the spectrum decreased with rising temperature although decomposition of MAIB should be accelerated at higher temperatures. This fact indicates that polymer radical II undergoes fragmentation much more easily at higher temperatures [equation (3)]. The system of MMA/MAIB/ETBA/benzene gave quite similar results.

The rate determining step of the chain transfer reaction is the addition of a propagating polymer radical to EBSA or ETSA. Since EBSA and ETSA are electron-accepting acrylate monomers, it is reasonable that these chain transfer reagents show a higher C_T value for St than for MMA and BA. The presence of EBSA or ETSA exerted little influence on the polymerization rate of the monomers, indicating that the eliminated arenesulfonyl radicals can effectively reinitiate the polymerization [equation (4)] [13].

As described above the α-arenesulfonylmethylacrylate esters are conjugative vinyl monomers though they can yield no polymer in radical polymerization. So, the system of MAIB/ethyl α-arenesulfonylmethylacrylate is expected to yield a persistent radical even in the absence of MMA.

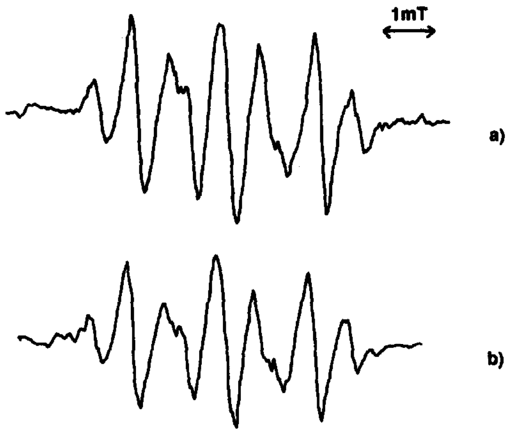
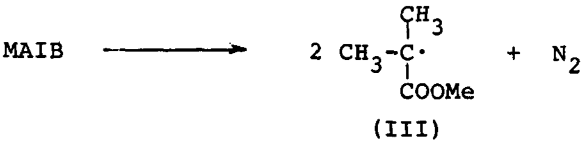


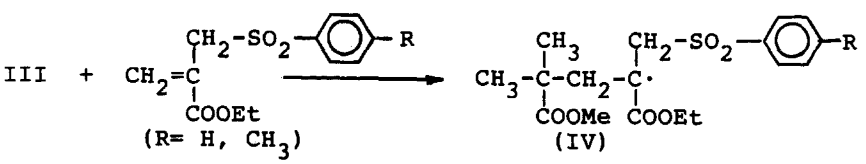
Fig. 5. ESR spectra of (a) MAIB/EBSA/toluene system and (b) MAIB/ETSA/toluene system under photoirradiation at room temperature.

Figure 5 shows the ESR spectra of the MAIB/EBSA and MAIB/ETBA systems observed under photoirradiation at room temperature as expected. The observed spectra are due to radical V1 formed by the following reactions:

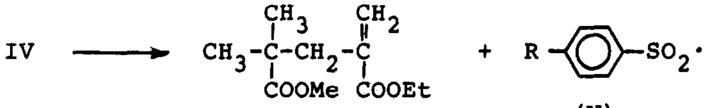


$$\text{MAIB} \longrightarrow 2\ \underset{\text{(III)}}{CH_3\text{-}\underset{|}{\overset{CH_3}{\overset{|}{C}}}\cdot} + N_2 \qquad (5)$$

(5)

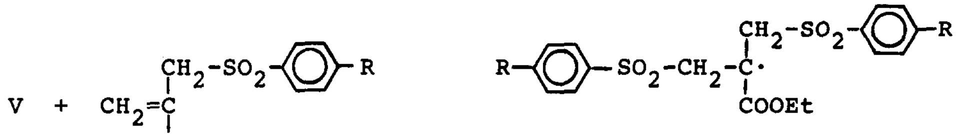


(6)



(V)

(7)

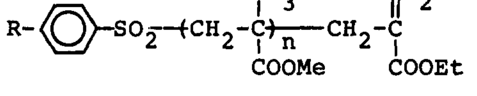


(VI)

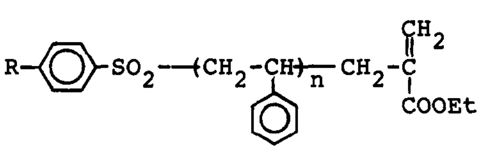
(8)

As mentioned above, when ethyl α-arenesulfonylmethylacrylates act as chain transfer reagents of addition-fragmentation type, the resulting polymers should carry a double bond at one terminal and an arenesulfonyl group at the other. To confirm the prediction, we have attempted to prepare poly(MMA) and poly(St) samples of low molecular weight by polymerization at a higher concentration of EBSA or ETSA. The results are listed in Table 3; the values of $\bar{M}_n$ were determined by GPC.

The structures of poly(MMA) and poly(St) above obtained are represented as VII and VIII.



(VII) (R= H, CH_3)



(VIII) (R= H, CH_3)

Table 3. Preparation of low molecular poly(MMA) and poly(St) samples by the polymerization at high concentration of ethyl α-arenesulfonylmethylacrylates (EASA)*

EASA	[EASA] (mol/l)	Monomer (M)	[M] (mol/l)	$\bar{M}_n$	$\overline{DP}_n$†
EBSA	0.50	MMA	3.76	2000	17.7
EBSA	0.50	St	3.46	820	5.4
ETSA	0.50	MMA	3.76	1600	13.3
ETSA	0.50	St	3.46	830	5.4

*[MAIB] = 1.00 × 10^{-2} mol/l, at 60°C, in benzene.

†$\overline{DP}_n$ was calculated by supposing $R—C_6H_4—SO_2—(M)_n—CH_2—\underset{\underset{CH_2}{\|}}{C}—CO_2Et$ (R=H, CH_3).

Figure 6 shows ^{1}H-NMR spectrum of poly(MMA) ($\overline{DP}_n$ = 17.7) obtained in the presence of EBSA. Absorptions at 5.42 and 6.17 ppm are ascribable to olefinic protons and those at 7.5–8.0 ppm to aromatic protons of the benzene sulfonyl group. Intensity ratio of signals due to olefinic protons and methoxy protons of MMA unit gave $\overline{DP}_n$ of 13. i.r. spectrum of the poly(MMA) sample also shows the presence of vinyl (1630 cm^{-1}) and phenyl groups (1600 cm^{-1}).

The ^{1}H-NMR spectrum of poly(St) presented in Fig. 7 shows signals due to olefinic protons at 5.09 and 5.92 ppm and also due to $—O—CH_2—$ group at the terminal at 3.9–4.2 ppm. $\overline{DP}_n$ = 5 was estimated by comparison of signal areas for olefinic and

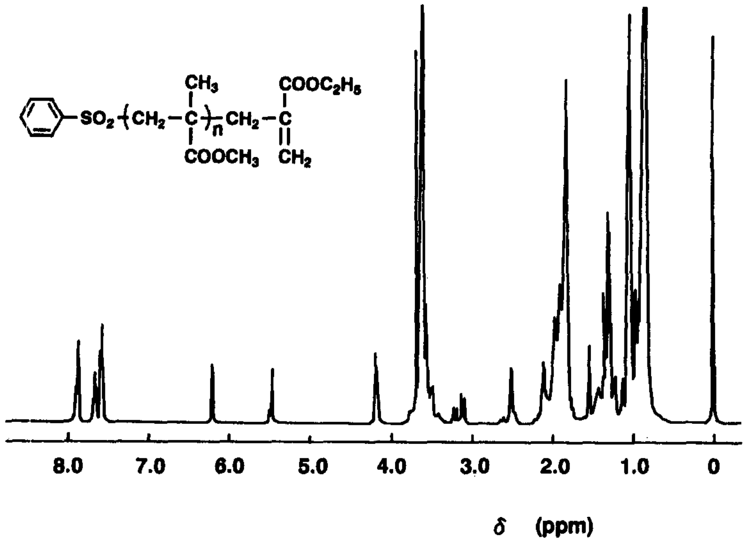


Fig. 6. ^{1}H-NMR spectrum of poly(MMA) formed in the polymerization in the presence of EBSA; [MMA] = 3.76 mol/l, [MAIB] = 1.0 × 10^{-2} mol/l, and [EBSA] = 0.5 mol/l.

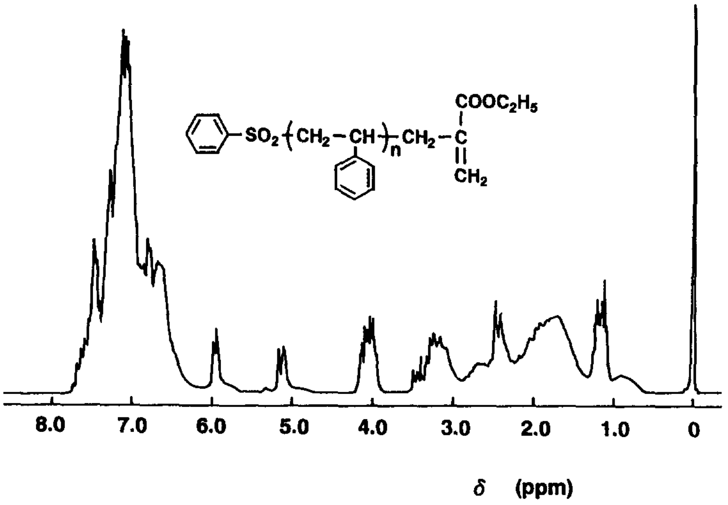


Fig. 7. ^{1}H-NMR spectrum of poly(St) formed in the polymerization in the presence of EBSA; [St] = 3.46 mol/l, [MAIB] = 1.0 × 10^{-2} mol/l, and [EBSA] = 0.5 mol/l.

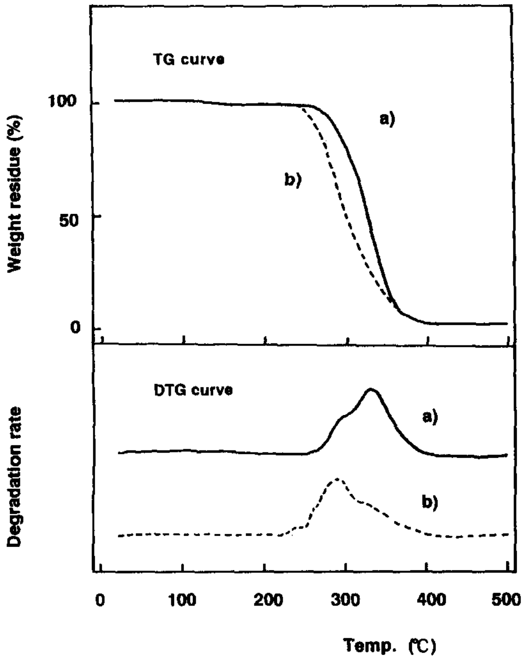


Fig. 8. TG and DTG curves of poly(MMA) formed (a) in the absence and (b) in the presence of EBSA; [EBSA] = 1.0 × 10^{-2} mol/l.

aromatic protons. The i.r. spectrum of the poly(St) sample revealed that the polymer has vinyl (1630 cm^{-1}) and carbonyl groups (1720 cm^{-1}).

Poly(MMA) and poly(St) samples formed in the presence of ETSA also gave similar spectroscopic results.

Figure 8 compares TG and differential thermogravimetric (DTG) curves of poly(MMA)s formed in the absence and presence (1.0 × 10^{-2} mol/l) of EBSA. Polymer formed in the presence of EBSA was thermally less stable than that formed in its absence. Similarly the presence of EBSA or ETSA led to poly(St) and poly(MMA) thermally less stable than those obtained without them.

CONCLUSIONS

EBSA and ETSA were easily prepared by the reactions of ethyl α-bromomethylacrylate with the sodium salts of benzene- and toluenesulfinic acids in acetone in the presence of tetrabutylammonium bromide as a phase transfer catalyst. EBSA and ETSA were found to act as effective chain transfer reagents in the polymerizations of MMA, St and BA, being conjugative monomers. An addition-fragmentation mechanism of the chain transfer reaction of EBSA and ETSA was confirmed by ESR studies of the polymerization system and by ^{1}H-NMR spectra and thermal behaviors of the resulting polymers.

On the other hand, EBSA acted as a retarder in the polymerization of VAc, a non-conjugative monomer.

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