

THE EFFECT OF POLAR ADDITIVES ON THE γ RADIATION INDUCED POLYMERIZATION OF STYRENE*

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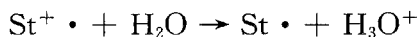
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ABSTRACT

The γ induced polymerization of styrene in the presence of polar additives such as tributyl phosphate, triethyl amine and ethanol was studied at dose rate of 5.0×10^{17} eV/ml. min. The result shows that radiation induced polymerization of styrene was sensitized by the three kinds of additives at the approximate same rate and the experimental results were in agreement with the theoretical calculation of WAS equation. The cause of sensitization is due to the proton transfer.

INTRODUCTION

Since the γ radiation initiated polymerization of styrene was accomplished successfully by Hopwood and Philips in 1938, the radiation polymerization of styrene has been studied extensively^[2-6]. Both free radical mechanism and cationic mechanism of polymerization of styrene have been found. It is well established that styrene proceeds cation polymerization under special experimental conditions such as "absolute dry" or "super dry" styrene, and using massive dose rate. The "normal dry" styrene, however, is polymerized by the free radical mechanism due to the proton transfer between $\text{St}^+ \cdot$ and H_2O to form initiator $\text{St} \cdot$.



Recently, Silverman and his coworkers^[7] studied the mechanism of radiation polymerization of styrene by using methanol as an additive but the results were too ambiguous to make clear the mechanism very well.

In this work, the effects of protophilic polar additives, such as tributyl phosphate (TBP), triethyl amine (TEA) and ethanol (Et), on the γ radiation polymerization of styrene have been studied. The initiated free radical yield (G value) is obtained by using gravimetric method to determine the polymerization rate of styrene and gel permeation chromatography (GPC) to measure the molecular weight distribution of polystyrene. The results show that all of these three additives are able to sensitize the radiation polymeriza-

tion of styrene at almost the same rate and is well in agreement with WAS equation. Therefore, it can be concluded that the energy transfer is mainly resulted from the proton transfer in the ST/TBP, ST/TEA and ST/Et system.

EXPERIMENTAL

1. Reagents

(1) Styrene (ST): AR grade, before using, it was washed three times with 10% NaOH and several times with distilled water until neutral, then dehydrated for 24 hours, distilled under 133.3 Pa and collected the distillates in the range of 22°C–23°C. It is necessary to note that purified styrene should be used immediately after distillation.

(2) Tributyl phosphate (TBP): AR grade, it was washed with 0.2 mol. dm⁻³ nitric acid and 1.0 mol. dm⁻³ NaOH three times respectively, then distilled under 133.3 Pa and the distillates in the range of 119–120°C were collected.

(3) Triethyl amine (TEA): AR grade, it was distilled and the distillates in the range of 89°C–90°C were collected.

(4) Anhydrous ethanol (Et): GR grade, it was dehydrated with anhydrous sodium sulfate sufficiently then distilled and the distillates in the range of 78–79°C were collected.

2. Irradiation condition

1.0 × 10¹⁴ bq Co⁶⁰ γ ray source, dose rate $\dot{D} = 1.33 \text{ Gy. s}^{-1}$ without otherwise stressed, the absorbed dose was measured by Fricke dosimeter wherein $G_{\text{Fe}^{3+}} = 15.5$.

The sample is bubbled with high purity nitrogen (99.999%) for 25 min. before sealed with gas flame under nitrogen atmosphere, then irradiated.

3. Measurement

(1) The determination of radiation polymerization rate (R_p)

Using gravimetric method to determine the rate of conversion of styrene into polystyrene, calculated as the following equation:

$$R_p = \frac{W_p}{M \cdot V \cdot t} (\text{mol. dm}^{-3} \cdot \text{s}^{-1})$$

where M is the molecular weight of styrene, V is the volume of styrene (dm³) in the irradiation tube, t is the irradiation time(s), W_p is the total weight of polystyrene (g). The polystyrene formed from the irradiated styrene was precipitated out, then was filtrated with sintered glass funnel

and washed with chilled methanol several times and evaporated to dryness, then put it in electric vacuum oven at approximate 50°C to reach constant weight W_p (g).

(2) The measurement of number average molecular weight $\overline{M}_n$.

The number average molecular weight was obtained with Vista-401 HPLC filled with gel permeation column from Varian Co.. The standard polystyrene was from Jilin University. Tetrahydrofuran was taken as eluant. The flow rate was 1.0 ml/min.. UV-detector was used.

RESULTS AND DISCUSSION

(1) The effects of protophilic polar additives, TBP, TEA and Et, on the rate of polymerization of styrene (R_p) are shown in Fig. 1.

As illustrated in Fig. 1 all of the three additives have similar sensitization effects on the radiation polymerization of styrene.

(2) The effects of TBP, TEA and Et on the number average molecular weight ($\overline{M}_n$) of polystyrene.

As shown in Table 1, the number average molecular weight of polystyrene decreases as increasing the concentration of these additives as TBP, TEA and Et, the protophilic additives behave as chain transferer and then lead to decrease the number average molecular weight of polystyrene.

Table 1 The effect of TBP, TEA and Et on the number average molecular weight of radiation induced polystyrene

Add. \ $C(\text{mol} \cdot \text{L}^{-1})$ $\overline{M}_n$							
	0.0	0.1	0.2	0.3	0.4	0.5	0.6
TBP	45741	44534	41418	38077	37342		
TEA	45741	43636	39011		35885	34531	
Et	45741	43947	42857		35166		33892

In the present work, the polymerization of styrene should follow free radical mechanism due to the fact that the styrene was not "absolute dry" or "super dry" and the polymerization proceeded at room temperature. In the presence of TBP, TEA and Et in styrene, the relationship between R_p and $\dot{D}^{1/2}$ is linear, as described in Fig. 2, the free radical mechanism is followed also^[1].

(3) The dependence of free radical yield (G) initiating the polymerization on the concentration of polar additives.

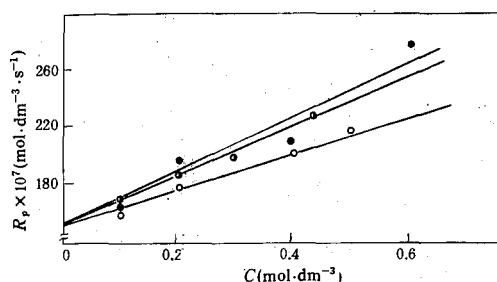


Fig. 1 The effect of TBP, TEA and Et on the radiation polymerization rate of styrene
 ● TBP ○ TEA ● Et
 dose rate: $1.33 \text{ Gy} \cdot \text{s}^{-1}$

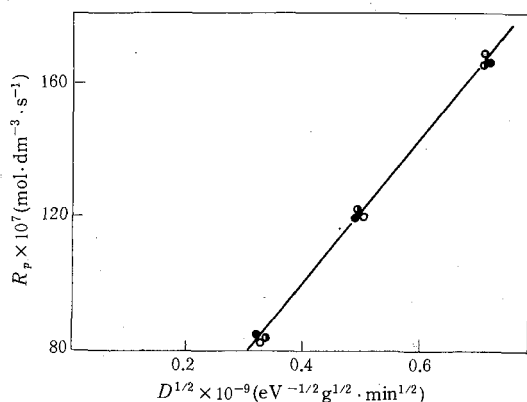


Fig. 2 The dependence of polymerization rate on the square root of dose rate ● TBP
 ○ TEA ● Et

Since these systems obey free radical mechanism, free radical yield (G) can be calculated as follows:

$$G = \frac{2N_0 \times Rp \times 100}{\bar{M}_n / M_{st} \times \dot{D} \times 1000}$$

wherein, Rp is polymerization rate ($\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$), $\bar{M}_n$ is the number average molecular weight of polystyrene, M_{st} is molecular weight of styrene, $\dot{D}$ is the dose rate ($\text{Gy} \cdot \text{s}^{-1}$), N_0 is Avogadro constant. Substituting the data into the formula above the G value was obtained as:

$$G = 1.5 \times 10^9 \frac{Rp}{\bar{M}_n}$$

It is predicted from the above equation that the free radical yield (G) should increase with increasing concentrations of additives, regarding the Rp increasing shown in Fig. 1 and $\bar{M}_n$ decreasing listed in Table 1. The G values of free radical are listed in Table 2.

Table 2 The dependence of G values of initial radicals on the concentrations of additives

$C(\text{mol} \cdot \text{L}^{-1})$ G								
		0.0	0.1	0.2	0.3	0.4	0.5	0.6
Add.								
TBP		0.49	0.57	0.67	0.78	0.89		
TEA		0.49	0.55	0.79		0.85	0.96	
Et		0.419	0.57	0.70		0.90		1.15

(4) The sensitization mechanism of styrene polymerization by protophilic polar additives.

It is well known that the ionization potential of TBP, TEA and Et is higher than that of styrene, so the charge transfer from styrene cationic radical to these three additives is not carried out. As TBP, TEA and Et are protophilic the sensitization mechanism can be proposed as follows:



Reaction (2) can be described quantitatively with WAS equation^[8].

$$G = G_{fi} + G_{gi} \frac{(\alpha S)^{1/2}}{1 + (\alpha S)^{1/2}} \quad (a)$$

where, G is the free radical yield of styrene, which is produced when the concentration of cation scavenger is S ; G_{fi} is the free ion yield of styrene; G_{gi} is the geminate ion yield of styrene.

Rearranging formula (a) into linear form:

$$\frac{1}{G - G_{fi}} = \frac{1}{G_{gi}} + \frac{1}{G_{gi}\alpha^{1/2}} S^{-1/2} \quad (b)$$

taking $G_{fi} = 0.1$, substituting data listed in Table 2 into formula (b) and making plot of $(G - G_{fi})^{-1}$

against $S^{-1/2}$ (Fig. 3 shows the relationship between $(G - G_{fi})^{-1}$ and concentrations of TBP, those of TEA and Et are excluded here due to the similar curves to that of TBP).

So that the values of G_{gi} and α can be obtained and listed in Table 3.

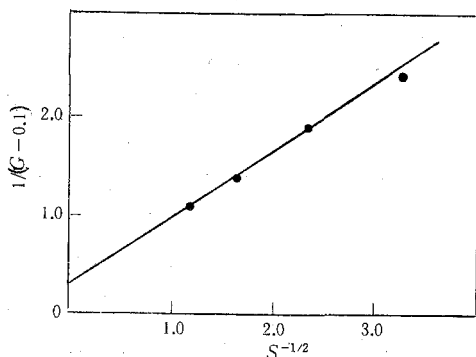


Fig. 3 $1/(G - 0.1)$ versus reciprocal square root of concentration of TBP

Table 3 The G_{fi} and G_{gi} values of styrene

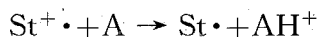
	α	G_{fi}	G_{gi}
TBP	0.14	0.1	4.0
TEA	0.14	0.1	4.0
Et	0.17	0.1	4.0

The results described in Table 3 have shown that the G value of geminate ion pair of styrene (G_{gi}) is coincident with each other.

Therefore, it is reasonable that the proton transfer processes occurs between styrene cation radical ($\text{ST}^{\cdot+}$) and molecule of polar additives.

CONCLUSION

The mechanisms of radiation polymerization of styrene, sensitized by protophilic polar additives, such as TBP, TEA and Et, are all proton transfer processes.



and the results fit WAS equation very well

$$G = G_{fi} + G_{gi} \frac{(\alpha S)^{1/2}}{1 + (\alpha S)^{1/2}}$$

the parameters in WAS equation calculated from the experimental data are $G_{fi} = 0.1$, $G_{gi} = 4.0$, $\alpha_{\text{St-TBP}} = 0.14$, $\alpha_{\text{St-TEA}} = 0.14$, $\alpha_{\text{St-Et}} = 0.17$, respectively.

Keywords:

Styrene; Induced polymerization; γ -radiolysis; Ethanol polar additives.

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