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ANALYSIS OF RADICAL OLIGOMERIZATION OF STYRENE BY FIELD DESORPTION MASS SPECTROMETRY

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The mechanism of thermally initiated polymerization of styrene has been investigated by field desorption mass spectrometry. Most of molecular ion peaks of styrene oligomers have been assigned to a few repetitive units of styrene with additive groups. As a result, it is concluded that the cleavage of styrene dimers to phenylpropenyl and benzyl radicals should contribute to the chain transfer and the reinitiation mechanisms of styrene polymerization.

The mechanism of radical polymerization was mainly discussed on the basis of kinetic studies. As a kind of analytical approach for this purpose, the tracer technique in use of a radioactive or stable isotope was examined by Bevington,1) and Kopecky and Evani.2) However, since synthetic oligomers or polymers usually consist of homologous mixtures, it is impossible to separate and identify each component of them by means of any conventional analytical method. On the other hand, the field desorption mass spectrometry (FD-MS), by which molecular weights of non-vaporized compounds can be determined, has been proposed as a powerful method to give only molecular ion peaks of oligomers with no cleavage of chemical bonds.3) In this paper, we have measured the FD-MS spectra of styrene oligomers synthesized in various alkyl benzenes, and discussed the reaction mechanism of thermally initiated polymerization of styrene.

In our experiment, the thermal oligomerization of styrene was carried out by heating in the sealed glass tubes containing styrene and solvent (molar ratio of 1/100) at 200°C for 2 h. The solvents used here were four alkyl benzenes; toluene, ethylbenzene, propylbenzene, and isopropylbenzene. The molecular weights of the oligomers obtained under such conditions were controlled to be below 1200. All FD-MS

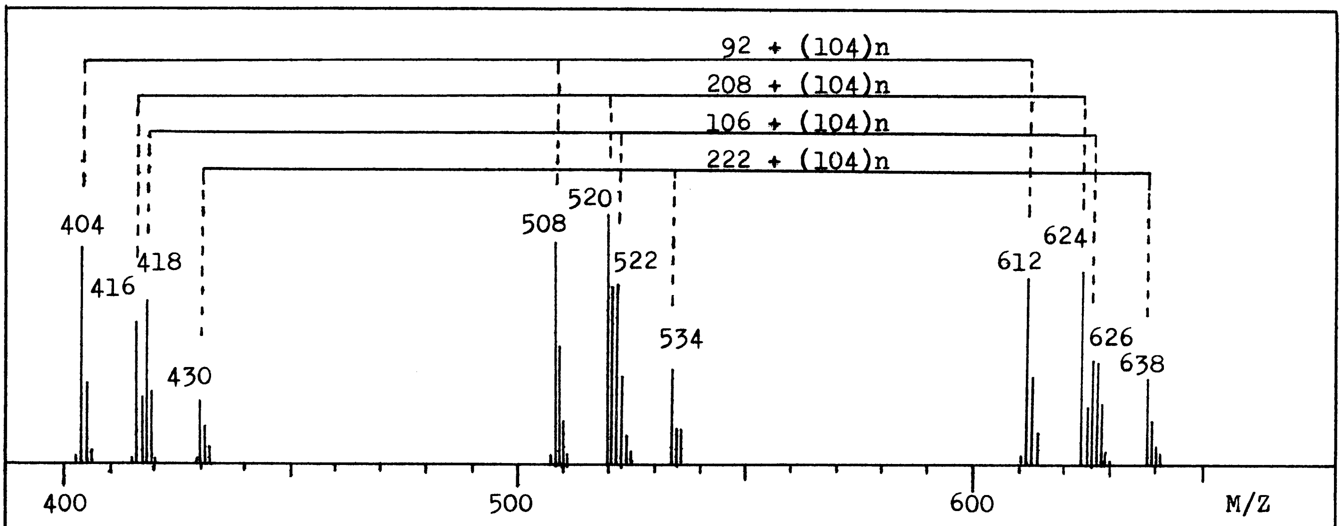
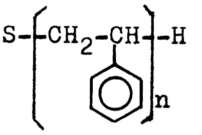


Fig.1 FD-MS spectrum of styrene oligomers synthesized in ethylbenzene

spectra were measured with the instrument described previously.[3)]

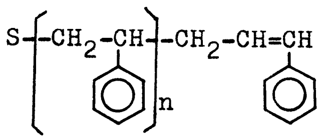
Figure 1 shows the FD-MS spectrum of styrene oligomers synthesized in ethylbenzene. It is seen from Fig.1 that four series of molecular ion peak patterns are distinguished by the mass number, 104, which is the repetitive unit interval of styrene. Then, these are generally formulated as "K+104n", where K is a constant and n is an integer corresponding to the degree of polymerization. The K's were estimated as 92, 106, 208, and 222 for four series, respectively.

Figure 2 shows the FD-MS spectra in the M/Z 500 to 600 region for styrene oligomers synthesized in toluene, propylbenzene, and isopropylbenzene. Each oligomer peak in Fig.2 is also classified in the above-mentioned way. These results are summerized individually in Table 1. From the obtained molecular weights, their chemical structures are possibly considered as follows;



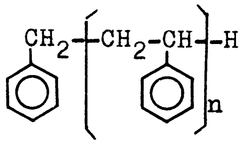
$S\text{-}\left[CH_2\text{-}CH(C_6H_5)\right]_n\text{-}H$

(1)



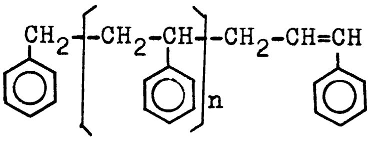
$S\text{-}\left[CH_2\text{-}CH(C_6H_5)\right]_n\text{-}CH_2\text{-}CH{=}CH(C_6H_5)$

(2)



$C_6H_5CH_2\text{-}\left[CH_2\text{-}CH(C_6H_5)\right]_n\text{-}H$

(3)



$C_6H_5CH_2\text{-}\left[CH_2\text{-}CH(C_6H_5)\right]_n\text{-}CH_2\text{-}CH{=}CH(C_6H_5)$

(4)

The appearance of species (1)-(4) could be explained by assuming that the chain transfer reactions of initiating or propagating radicals to styrene dimers (SD) and solvents (SH), as shown in (5)-(8), play an important role in the whole reaction process. They may be probably supported from the fact that the chain

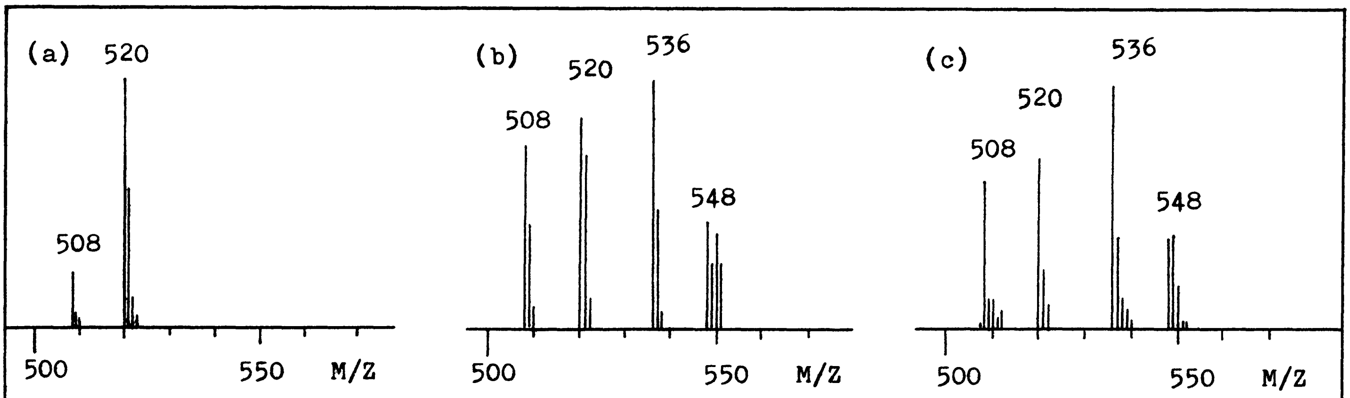


Fig.2 FD-MS spectra (M/Z: 500-570) of styrene oligomers synthesized in various solvents. (a) toluene, (b) propylbenzene, (c) isopropylbenzene

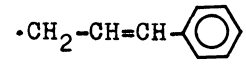
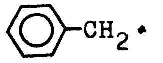
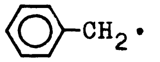
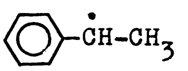
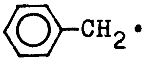
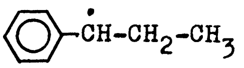
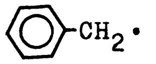
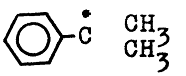
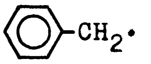
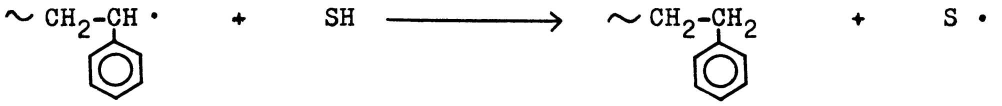
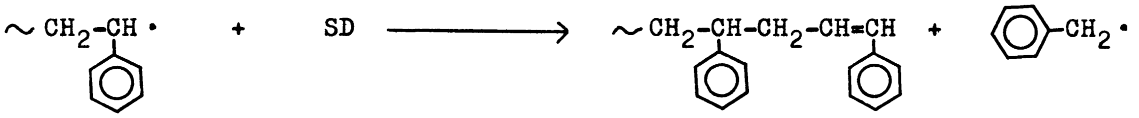
SOLVENT	HEAD GROUP / TAIL GROUP	•H	
TOLUENE	 91	$92 + (104)_n$	$208 + (104)_n$
	 91	$92 + (104)_n$	$208 + (104)_n$
ETHYLBENZENE	 105	$105 + (104)_n$	$222 + (104)_n$
	 91	$92 + (104)_n$	$208 + (104)_n$
PROPYLBENZENE	 119	$120 + (104)_n$	$236 + (104)_n$
	 91	$92 + (104)_n$	$208 + (104)_n$
Isopropylbenzene	 119	$120 + (104)_n$	$236 + (104)_n$
	 91	$92 + (104_n$	$208 + (104)_n$

Table 1 The summary of the species derived from the proposed mechanism

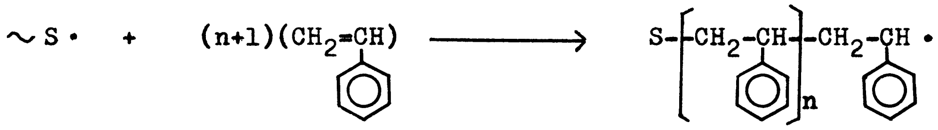
transfer constant to the SD in the thermal polymerization of styrene is 10^2-10^3 times higher than it to any hydrocarbon solvent used here, which was pointed out by Pryor and Coco,[4)] but under our experimental conditions, the chain transfer to the solvent could occur with a rather high probability, because of the low concentration of styrene monomers (below 1 mol%). As a result, it is suggested that in addition to solvents both benzyl and phenylpropenyl radicals produced with the cleavage of SD should contribute to the mechanism of thermal oligomerization of styrene. Moreover, it is clarified that phenylpropenyl radicals should work only for the terminating



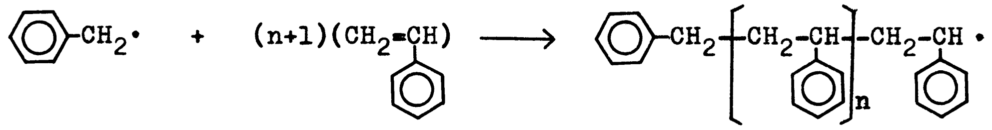
$\sim CH_2\text{-}CH(C_6H_5)\cdot + SH \longrightarrow \sim CH_2\text{-}CH_2(C_6H_5) + S\cdot$ (5)



$\sim CH_2\text{-}CH(C_6H_5)\cdot + SD \longrightarrow \sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH{=}CH(C_6H_5) + C_6H_5\text{-}CH_2\cdot$ (6)

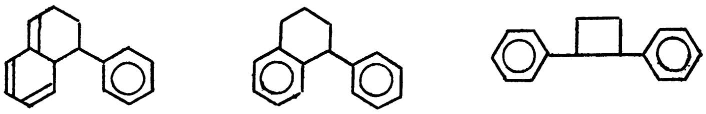


$\sim S\cdot + (n+1)(CH_2{=}CH(C_6H_5)) \longrightarrow S\text{-}[CH_2\text{-}CH(C_6H_5)]_n\text{-}CH_2\text{-}CH(C_6H_5)\cdot$ (7)



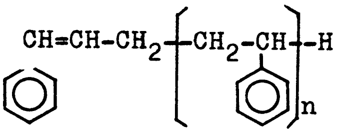
$C_6H_5\text{-}CH_2\cdot + (n+1)(CH_2{=}CH(C_6H_5)) \longrightarrow C_6H_5\text{-}CH_2\text{-}[CH_2\text{-}CH(C_6H_5)]_n\text{-}CH_2\text{-}CH(C_6H_5)\cdot$ (8)

SD :



etc.

process, since the chemical species as shown in (9) have not been observed in all FD-MS spectra, in spite of the appearance of (2) and (3).



$CH{=}CH(C_6H_5)\text{-}CH_2\text{-}[CH_2\text{-}CH(C_6H_5)]_n\text{-}H$ (9)

In conclusion, it is found that the FD-MS can be applied to the analysis of the oligomerization mechanism. Particularly, in the case of the application of FD-MS to the analysis of the thermal polymerization of styrene, it can be clarified for the first time that the phenylpropenyl radicals from SD's contribute to the terminating mechanism of the polymerization. In relation to the above-mentioned considerations, further experimental investigations, for example, using deuterated styrene monomers are required.

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