

Analysis of Thermal Oligomerization Mechanism of Styrene by Field Desorption Mass Spectrometry

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Synopsis

Field desorption mass spectra of normal and deuterated styrene oligomers synthesized in several alkylbenzenes were measured. Analysis of the mechanism of thermal oligomerization was carried out by identifying the molecular species in the reaction system using field desorption mass spectra. As a result, the existence of several kinds of molecular species was confirmed. The minor molecular species originated from dissolved oxygen, from the cleavage of solvent radicals to which oxygen was attached, or from H-D exchange in the oligomerization of deuterated styrene. The major molecular species originated from radical telomerization of solvents and styrene dimers, from the recombination termination reaction, and from the cage reaction between initiating radicals. Field desorption mass spectrometry was found to be useful for analyzing the mechanism of styrene oligomerization as well as characterizing the oligomers.

INTRODUCTION

Recent investigations¹⁻⁸ have shown the usefulness of field desorption mass spectrometry (FDMS) for determining molecular weights of nonvolatile samples such as synthetic polymers. As an advantage of FDMS, it has been demonstrated¹⁻³ that FDMS is a powerful analytical method which normally gives molecular ions as the strongest peaks without noticeable fragment ion peaks. On the basis of the above-mentioned potentialities, FDMS has been applied to the measurements of molecular weight distributions of various kinds of polymers¹⁻⁴ and to the characterization of synthetic polymers.⁵⁻⁸

In the course of our studies on FDMS of polymers, we have considered the mechanism of radical telomerization⁶⁻⁸ in which solution polymerization of styrene is initiated thermally and propagated through chain transfer reactions. In the case of free radical polymerization such as thermal polymerization of styrene, the structures of repeating units of the synthesized polymers have been well characterized. Few studies, however, have been reported about the structural elucidation of the head and tail groups of the polymer, although valuable information on the mechanism of polymerization can be deduced from the precise identification of those groups. This situation may be due to the fact that the structural investigations of polymers often require troublesome and difficult analytical procedures. FDMS, on the other hand, has the potential ability to

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facilitate these analyses. By means of FDMS, it has been shown previously⁸ that the chain transfer reaction of the growing chain radical to the Diels–Alder adduct intermediates as well as the solvent molecules plays an important part in the formation of styrene oligomers by thermal polymerization.

In the present investigation, detailed analysis of the molecular species observed in FDMS spectra of styrene oligomers synthesized in several aromatic solvents was carried out in order to examine the mechanism of thermal polymerization. The effects of dissolved oxygen radicals, cleavage radicals of solvent molecules, and cleavage radicals of Diels–Alder adduct intermediates on the polymerization are also examined.

EXPERIMENTAL

Normal (vinyl- d_0) styrene monomer, propylbenzene, isopropylbenzene, butylbenzene, and *s*-butylbenzene were commercially obtained and were purified by distillation just before use. Deuterated (vinyl- d_3) styrene with an enrichment of 98% was purchased from Merck Sharp and Dohml, Ltd. and was used without further purification.

The thermal polymerization was carried out by heating the sealed glass tube in which d_0 or d_3 styrene was dissolved in a solvent at the molar ratio of 1/100. As the first step, the reaction tube was cooled at dry ice–methanol temperature, was degassed *in vacuo* for ca. 3 min; and then it was sealed. Subsequently, the tube was heated at 200°C for 2 h. After the polymerization was terminated, solvents in the reaction tube were allowed to evaporate, and the residual styrene oligomers were dissolved in chloroform and analyzed by FDMS.

FDMS spectra were measured on a JEOL Model JMS DX-300 Double Focusing Mass Spectrometer. The samples were loaded on a carbon emitter with a 10- μm diameter. Measurement conditions were as follows: The temperature of the ion source was 50°C. Mass spectral resolution ($M/\Delta M$) was 1000. Accelerating and cathode voltages were 3.0 kV and –5.5 kV, respectively. Magnetic field scanning speed was 50–1000 amu/10 s. The emitter current was increased from 0 to 25 mA at the rate of 1 mA/min. Output signal from the mass spec-

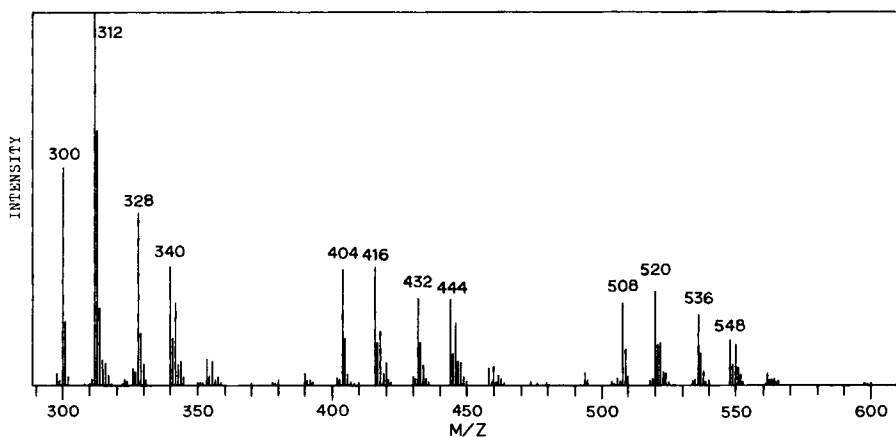


Fig. 1. FDMS spectrum of styrene oligomers synthesized in propylbenzene.

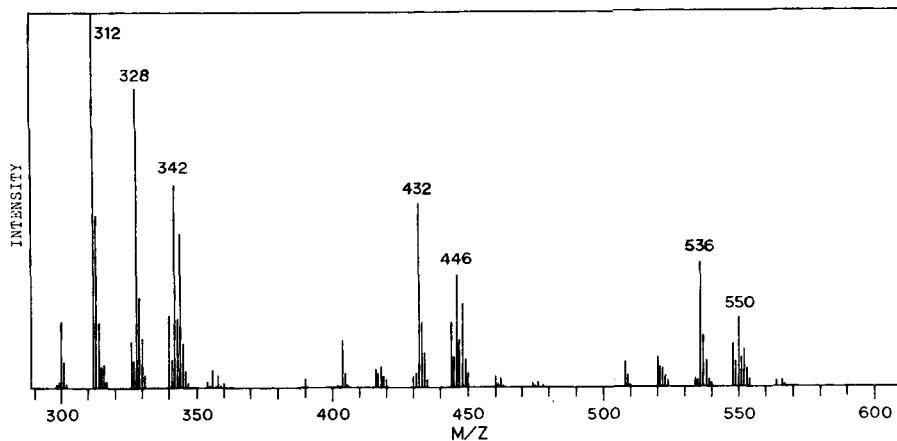


Fig. 2. FDMS spectrum of styrene oligomers synthesized in isopropylbenzene.

trometer was processed by a JEOL JMA-3500 Data Processing System. Mass numbers were calibrated with perfluorokerosene and poly(perfluoropropylene oxide) in EI mode.

RESULTS AND DISCUSSION

FDMS spectra of d_0 and d_3 styrene oligomers synthesized in various solvents—propylbenzene, isopropylbenzene, butylbenzene, and *s*-butylbenzene—are shown in Figures 1–8. It is immediately seen from Figures 1–4 that the spectra of d_0 styrene oligomers give several series of peaks at 104 amu intervals. As for the d_3 styrene oligomers, several series of peaks appearing at 107 amu intervals are observed in the FDMS spectra (Figs. 5–8). The mass numbers of 104 and 107 correspond to those of the repeating units of the d_0 and the d_3 polystyrenes, respectively. These peaks can be related to molecular species which have a head group, a tail group, and several repeating units. Accordingly, the mass numbers of these molecular species can be expressed gen-

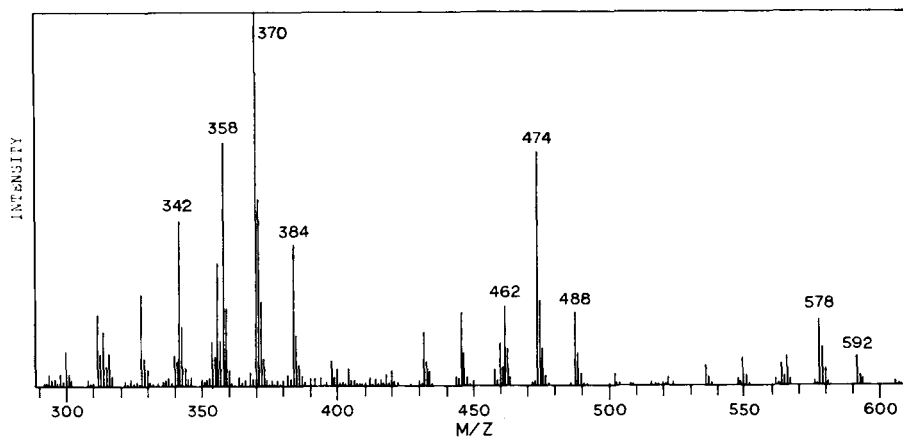


Fig. 3. FDMS spectrum of styrene oligomers synthesized in butylbenzene.

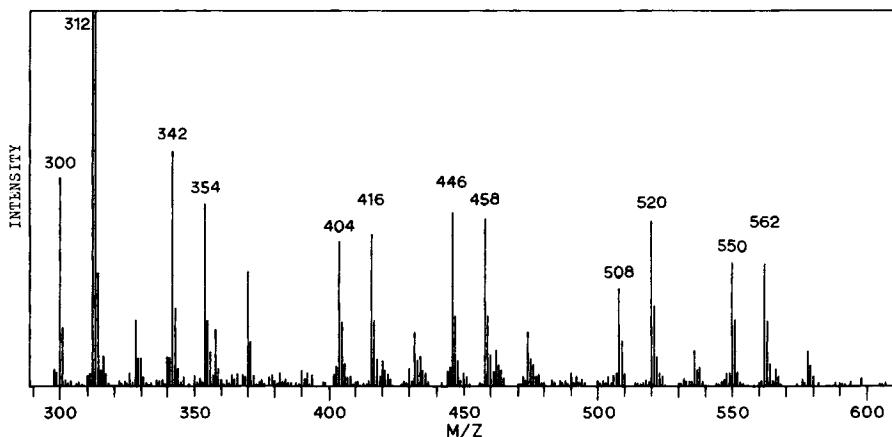


Fig. 4. FDMS spectrum of styrene oligomers synthesized in *s*-butylbenzene.

erally as " $K + 104n$ " and " $K + 107n$ " for d_0 and d_3 styrene oligomers, respectively. In the above expression, n represents an integer and K the summed mass number of the head and the tail groups.

For the initiation mechanism in the thermal polymerization of styrene, schemes have been proposed by Mayo,⁹ Kopecky and Evani,¹⁰ and many other authors, and these have been extensively accepted. The first step of the thermal polymerization is the formation of a Diels–Alder intermediate (SD: styrene dimer) produced by two styrene monomers as shown in eq. (1), where SD represents the intermediate such as 1-phenyl-1,2-dihydronaphthalene (A), 1-phenyltetralin (B), 1,2-diphenylcyclobutane (C) and so on. Successively, SD reacts with styrene monomer as shown in eq. (2), and the reaction produces two radicals which are the initiators for the thermal polymerization:

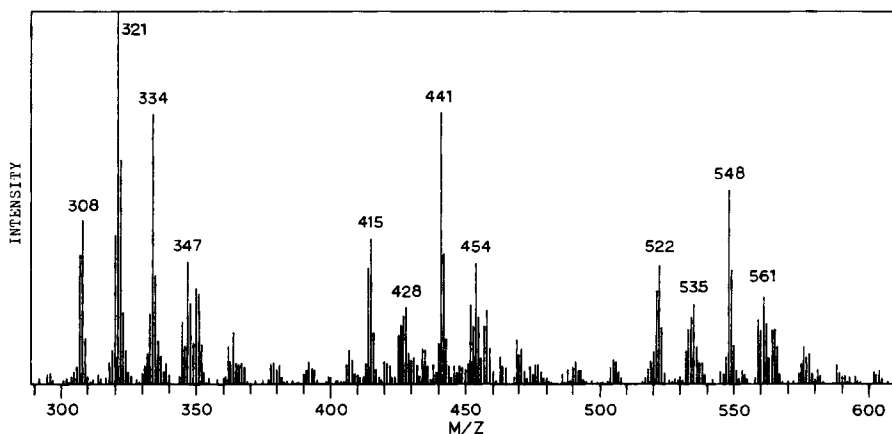
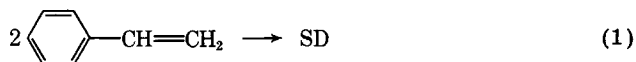


Fig. 5. FDMS spectrum of deuterated styrene oligomers synthesized in propylbenzene.

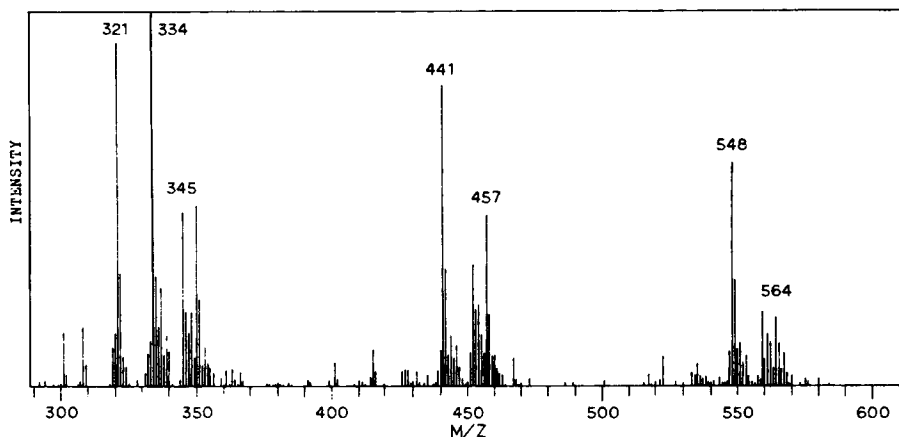
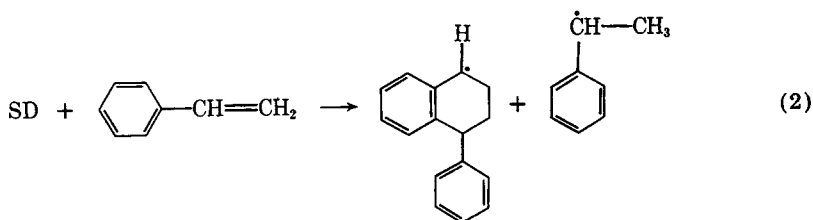


Fig. 6. FDMS spectrum of deuterated styrene oligomers synthesized in isopropylbenzene.



Although the initiation reaction can result from species (A), the chain transfer reaction can not be said conclusively to be caused by species (A) only. In addition to (A), species (B) and (C) can contribute in principle to the chain transfer reaction.

Under our synthetic conditions, the polymerization of styrene was carried out in a large excess of solvent. In such a case, it has been reported⁸ that the reaction schemes of eqs. (3)–(6) are dominant in the chain transfer process based on the mass spectral observation of the molecular species (I)–(VI).

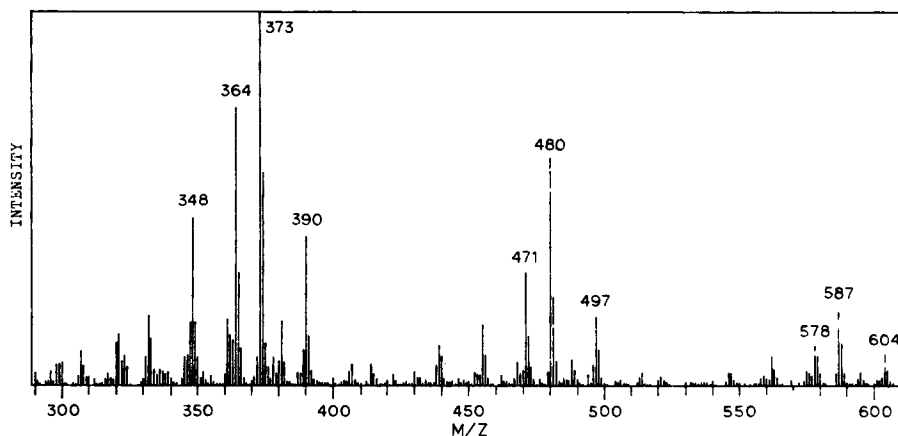


Fig. 7. FDMS spectrum of deuterated styrene oligomers synthesized in butylbenzene.

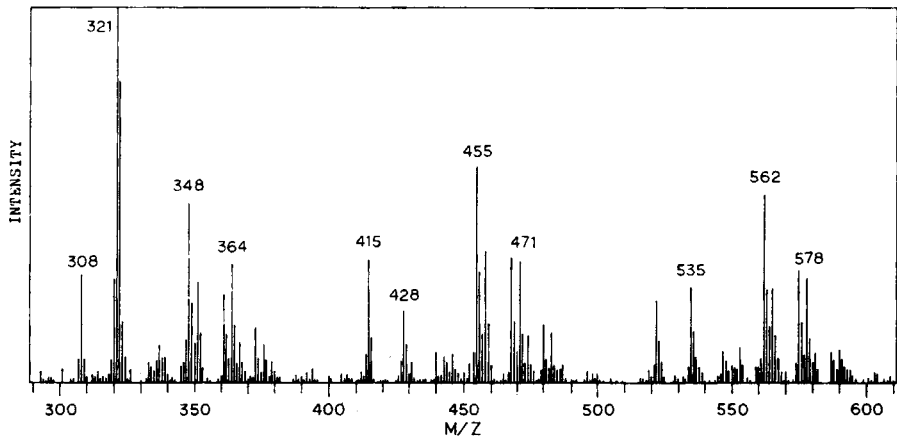
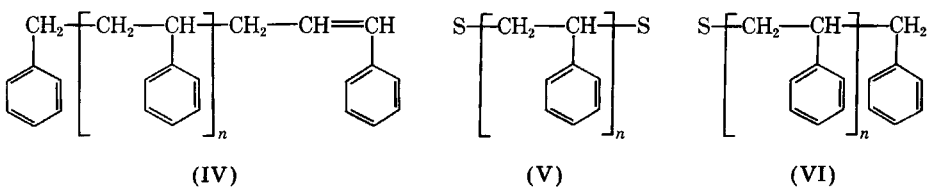
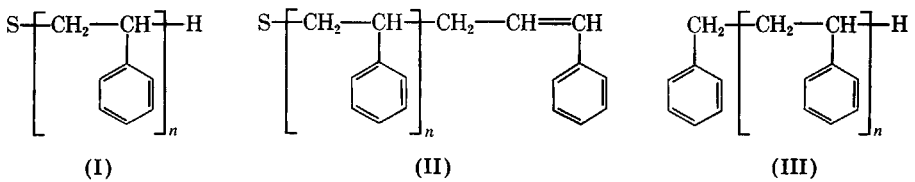
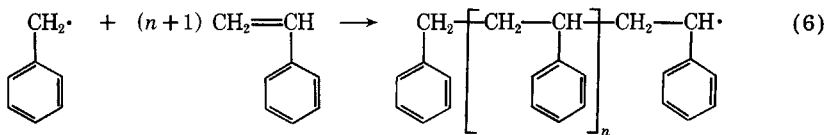
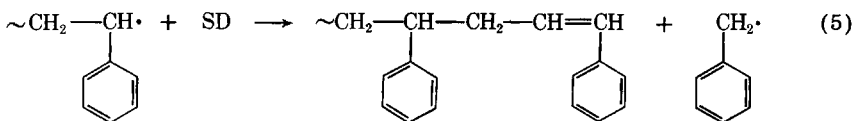
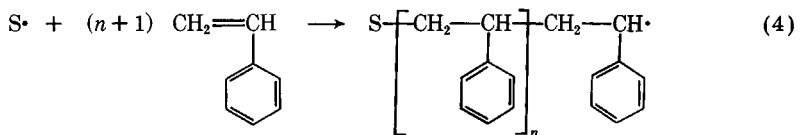
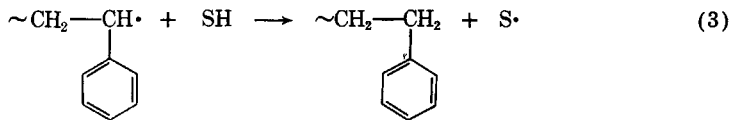
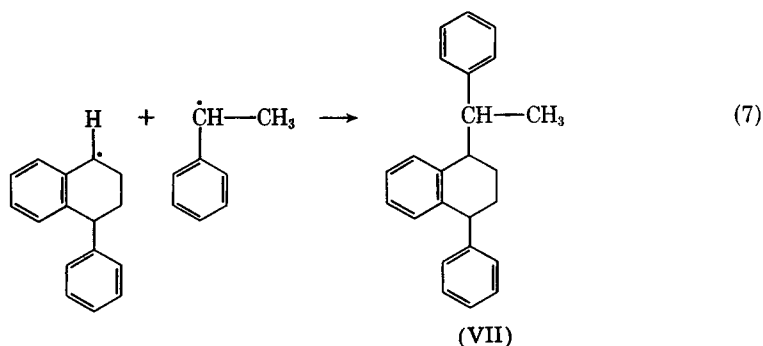


Fig. 8. FDMS spectrum of deuterated styrene oligomers synthesized in *s*-butylbenzene.



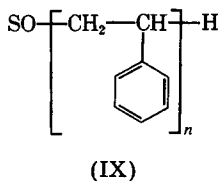
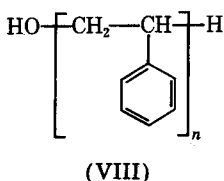
Furthermore, we have previously reported⁸ the existence of the trimeric styrene (VII) produced by the cage reaction [eq. (7)] between the two initiating radicals presented in eq. (2):



The above conclusions are also confirmed by the present investigation. The molecular weights of the species of (I)–(VI) can be formulated generally as “ $K + 104n$,” and the expected mass numbers for styrene oligomers synthesized in propylbenzene are summarized in Table I. Six series of the molecular species (I)–(VI) listed in Table I can be clearly recognized in the FDMS spectra shown in Figure 1. The trimeric species (VII) formed by the cage reaction is the base peak at m/z 312 in Figure 1. In the case of d_3 styrene oligomers, the trimeric species is observed at m/z 321 as shown in Figure 5.

The expected mass numbers for d_0 and d_3 styrene oligomers synthesized in several alkylbenzenes are summarized in Table II. All of the molecular species designated by the general formulas listed in Table II can be clearly seen in the FDMS spectra as shown in Figures 1–8.

On the other hand, one can see many additional peaks which cannot be assigned to the species of (I)–(VI) in the FDMS spectra. In order to classify the above unknown peaks, the FDMS spectra of d_0 and d_3 styrene oligomers synthesized in the same solvent have been compared with each other, and the FDMS spectra of styrene oligomers synthesized in the different solvents have also been compared with one another. Some of the additional molecular species contain an oxygen atom, and proposed structures are shown in (VIII) and (IX).



In (IX), SO represents a radical formed by the addition of oxygen atom to solvent molecule. The expected mass numbers of the species of (VIII) and (IX) are summarized in Table III, and the correct mass numbers can be observed in the FDMS spectra shown in Figures 1–8, although some of them have relatively low intensities.

Mass spectral observation of the molecular species of (VIII) and (IX) which

TABLE I
General Formulas and Expected Mass Numbers for Styrene Oligomers Synthesized in Propylbenzene





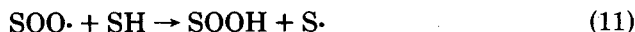
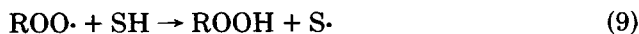
Head group	$\cdot\text{H}$	Tail group
	$m/z = 1$	
$\text{CH}-\text{CH}_2-\text{CH}_3$	$120 + 104n$	$\text{CH}_3-\text{CH}_2-\text{CH}$
$m/z = 119$	$m/z = 328, 432, 536$	$m/z = 119$
	$92 + 104n$	
$m/z = 91$	$m/z = 300, 404, 508$	$m/z = 117$
	structure (I)	structure (II)
	structure (III)	structure (IV)
		structure (V)
		structure (VI)

TABLE II
General Formulas for d_0 and d_3 Styrene Oligomers Synthesized in Alkylbenzenes

Structure	Solvent			
	Propylbenzene, Isopropylbenzene		Butylbenzene, <i>s</i> -Butylbenzene	
	Monomer: d_0 Styrene	d_3 Styrene	d_0 Styrene	d_3 Styrene
(I)	$120 + 104n$	$120 + 107n$	$134 + 104n$	$134 + 107n$
(II)	$236 + 104n$	$240 + 107n$	$250 + 104n$	$254 + 107n$
(III)	$92 + 104n$	$94 + 107n$	$92 + 104n$	$94 + 107n$
(IV)	$208 + 104n$	$214 + 107n$	$208 + 104n$	$214 + 107n$
(V)	$238 + 104n$	$238 + 107n$	$266 + 104n$	$266 + 107n$
(VI)	$210 + 104n$	$212 + 107n$	$224 + 104n$	$226 + 107n$

have OH and SO end groups suggests that these two species may be caused by OH and SO radicals. With oxygen in the reaction system, the above two radicals may be produced by the following reaction schemes:



where $R\cdot$ represents the initiation radical shown in eq. (2) and SH represents a solvent molecule. According to eqs. (10) and (11), $SOOH$ can be produced repeatedly until the dissolved oxygen molecules are consumed. The final amount of $SOOH$, therefore, can be greater than that of $ROOH$. SO and HO radicals are produced by eq. (12), and react with styrene monomers as shown in eqs. (13) and (14):

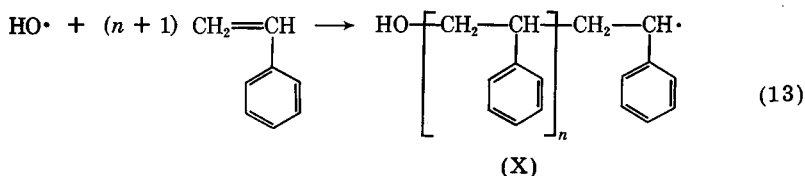
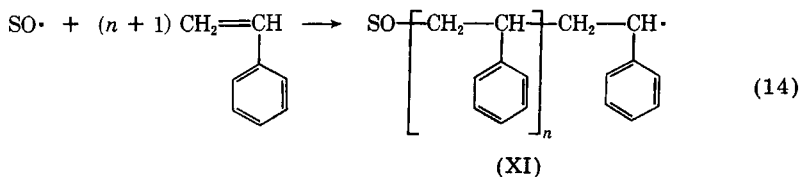


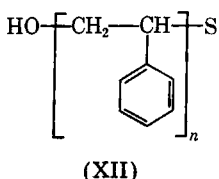
TABLE III
General Formulas and Expected Mass Numbers of Styrene Oligomers

Solvent	Monomer	Structure	
		(VIII)	(IX)
Propylbenzene	d_0 styrene	$18 + 104n$	$136 + 104n$
		$m/z = 330, 434, 538$	$m/z = 344, 448, 552$
Isopropylbenzene	d_3 styrene	$18 + 107n$	$136 + 107n$
		$m/z = 339, 446, 553$	$m/z = 350, 457, 564$
Butylbenzene	d_0 styrene	$18 + 104n$	$150 + 104n$
		$m/z = 330, 434, 538$	$m/z = 358, 462, 566$
<i>s</i> -Butylbenzene	d_3 styrene	$18 + 107n$	$150 + 107n$
		$m/z = 339, 446, 553$	$m/z = 364, 471, 578$

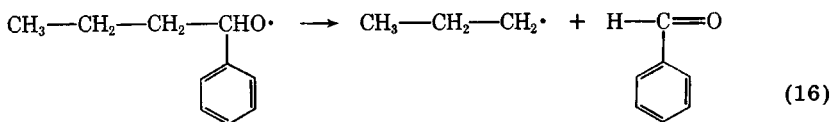
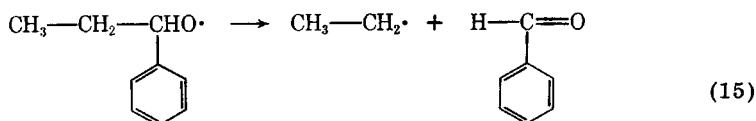


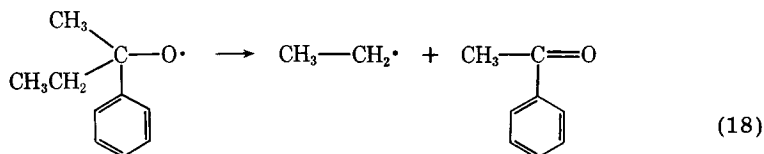
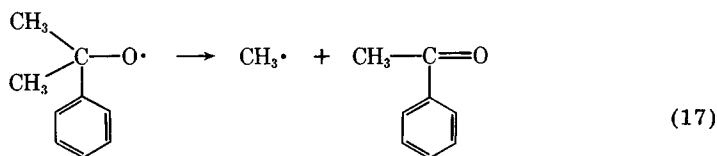
Molecular species of (VIII) and (IX) are proposed to be produced by the chain transfer reaction in which the growing chain radicals of (X) and (XI) abstract hydrogen from solvent molecules. On the other hand, there is some possibility that the growing chain radicals (X, XI) react with other chemical species through a chain transfer reaction or a recombination reaction. In this case, other molecular species than the ones designated in (VIII) and (IX) may be produced. In fact, molecular species produced by the recombination reaction between the growing chain radicals (X) can be identified in the FDMS spectra, although their peak intensities are very weak.

Molecular species shown in (XII) may also be produced through the reactions with an oxygen molecule, although these species cannot be differentiated from the species shown in (IX):

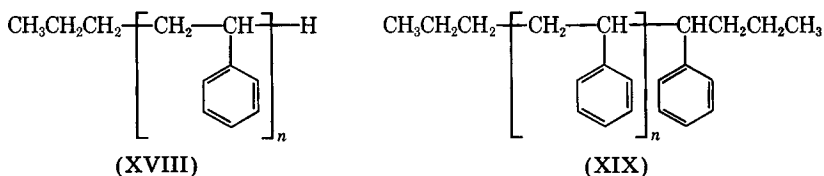
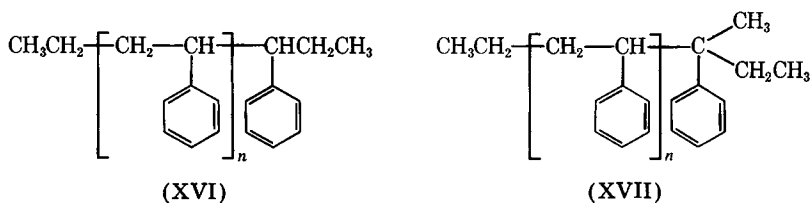
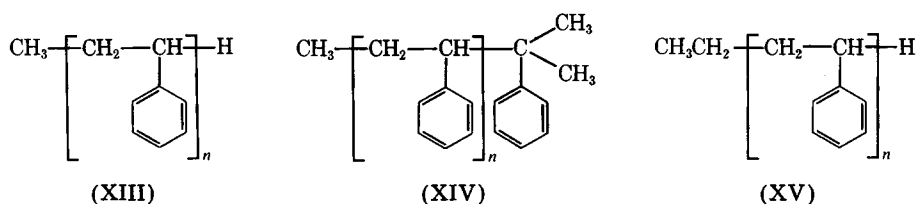


As shown in Figures 1-8, the peaks assigned to the molecular species of (VIII) and (IX) are observed with slightly different intensities in the FDMS spectra. This observation may be due to the difference of the initial concentration of the dissolved oxygen molecules. It is clear that the generation of the molecular species originating from oxygen depends on the concentration of dissolved oxygen in the reaction tube. Under the present degassing procedures, the same experimental conditions were not used for each polymerization. In addition to the molecular species produced by the growing chain radicals (X, XI), another type of molecular species which may form via the cleavage of SO radicals can be proposed. The cleavage of SO radicals can produce methyl, ethyl, or propyl radicals depending on the alkyl group of the aromatic solvents, as shown in the following reaction schemes:





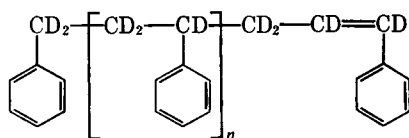
These alkyl radicals can produce the following molecular species shown below through the chain transfer or the recombination termination reactions:



The molecular species designated by (XIII) and (XIV) can be produced in the polymerization if isopropylbenzene is used as a solvent. The species (XV) can be produced by using propyl- or *s*-butylbenzenes as the solvent. Species (XVI) and (XVII) can be produced in the polymerization by using propylbenzene and *s*-butylbenzene, respectively, and the species (XVIII) and (XIX) can result from the butylbenzene solvent.

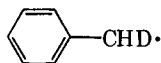
The above proposal is supported by the observation of species having methyl, ethyl, and propyl end groups. The general formulas as well as the expected and the observed mass numbers for the molecular species of (XIII)–(XIX) are summarized in Table IV.

On the other hand, differences can be found by comparing the FDMS spectra of d_3 styrene oligomers with those of d_0 styrene oligomers. That is, the former shows more peaks than the latter. This fact suggests that molecular species which are specific for d_3 styrenes may be formed in the synthesized oligomers. One possible reason for the above difference is that the cleavage of SD shown



(XXII)

Besides the above three species, species which are 1 amu lower than the species of (XX) and (XXI) can be expected to be produced, considering the reinitiation reaction with



As for the species of (XXII), 1 amu lower or higher species can be produced through the reaction shown in eq. (20). The general formulas for these molecular species are summarized in Table V. As shown in Figures 5–8, the 1 amu lower signals can be clearly observed. The 1 amu higher signals, however, are not always clear in the high mass region because of the ^{13}C isotope effect.

In conclusion, molecular species of d_0 and d_3 styrene oligomers polymerized thermally in several aromatic solvents have been characterized by means of FDMS. As a result, the existence of several kinds of molecular species in the reaction system has been identified by the observation of mass signals with characteristic mass numbers. Certain molecular species arise from effects of dissolved oxygen, from the cleavage of solvent radicals to which oxygen is attached, and from H–D exchange during the polymerization of d_3 styrene. Other molecular species originate from the radical telomerization of solvents and the SD's from the recombination termination reaction, and from the cage reaction between initiating radicals.

This is the first demonstration that the mechanisms of the thermal polymerization can be studied by identifying the molecular species in the reaction system using a FDMS technique. It has been found that methyl, ethyl, and propyl radicals are produced by the cleavage of the solvent radicals to which oxygen is attached. These results suggest that FDMS can give valuable insight regarding reaction mechanisms.

TABLE V
General Formulas and Observed Mass Numbers of Styrene Oligomers

Structure	General formulas	Observed mass numbers
(XX)	$93 + 107n$	$m/z = 307, 414, 521$
	$94 + 107n$	$m/z = 308, 415, 522$
(XXI) propyl group	$211 + 107n$	$m/z = 318, 425, 522$
	$212 + 107n$	$m/z = 319, 426, 533$
butyl group	$225 + 107n$	$m/z = 332, 439, 546$
	$226 + 107n$	$m/z = 333, 440, 547$
(XXII)	$213 + 107n$	$m/z = 320, 427, 534$
	$214 + 107n$	$m/z = 321, 428, 535$
	$215 + 107n$	$m/z = 322, 429, 536$

One can see, however, several weak signals in the FDMS spectra, which cannot be assigned at present. In order to obtain more detailed information, more experimental investigations are required, and the work is now continuing to clarify the unassigned signals.

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