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Analysis for the Oligomerization Mechanism of Styrene by Field Desorption Mass Spectrometry

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Measurements were made of field desorption mass spectra of normal and deuterated styrene oligomers synthesized in various alkylbenzenes. Several series of molecular ion peaks are observed in both the spectra. From a comparison between them we have identified oligomers' end groups and derived formation mechanisms for individual molecular species. It has been clarified that molecular species independent of solvents are produced through chain transfer of propagating radicals to styrene dimers. Analysis for the polymerization mechanism of styrene as well as characterization of polymer molecules has been successfully performed by field desorption mass spectrometry.

Field desorption mass spectrometry (FD-MS) has been recognized as a very powerful tool for determination of molecular weights and structural characterization of nonvolatile compounds.[1] Recently, FD-MS has been applied also to examining various synthetic oligomers or polymers which consist of homologous mixtures, and its potentials for characterizing polymers have been demostrated.[2—4] However, until now the applicability of FD-MS to polymer chemistry has been restricted to determination of molecular weight distributions and molecular species.

Bevington[5] proposed from results in kinetic studies that radicals generated through reaction of Diels-Alder adducts with styrene monomers should react as an initiator in the thermally initiated polymerization of styrene. Similar results were obtained in a study[6] with considerations of isotope effect in the case of deuterated styrene.

In our previous works using the FD-MS,[7,8] we discussed on the telomerization of styrene oligomers to a chain transfer agent of 1,1,3,3,5,5-hexamethylhexanethiol and identified molecular species generated by the chain transfer in the thermal polymerization. In this investigation, we have been able to analyze successfully the mechanism of the thermally-initiated polymerization of styrene on the basis of FD-MS spectra of normal and deuterated styrene oligomers.

Experimental

Sample Preparation. Normal styrene monomer, toluene, ethylbenzene, propylbenzene, and isopropylbenzene were all commercial chemicals and used after distillation. Deuterated styrene monomer was obtained from Merck Sharp & Dohme Co., Ltd. and used without purification.

The oligomerization of normal or deuterated styrene was carried out by heating a sealed glass tube containing normal or deuterated styrene in solvent (molar ratio 1/100) at 200 °C for 2 h.

Apparatus. Mass spectrometry was performed on a JEOL-JMS D-300 double focusing mass spectrometer with a combined field desorption/field ionization/electron impact ion source, connected to a JMA 2000S mass data analysis system. The FD emitter used was a 10 μm tungsten wire with carbon needles. The oligomer sample was dissolved in chloroform (about 1 mg/0.5 ml) and loaded on the emitter by the normal dipping technique. The calibration of magnetic field current was done with perfluorokerosene or perfluoropoly(propylene oxide) as the reference *via* the EI mode. The accelerating voltage was either 3 or 2 kV. The instrumental resolution, $M/\Delta M$, was *ca.* 1000 (10% valley). The emitter current was increased linearly in the range 0—25 mA at the rate of 2 mA/min. The cathode potential was 5.5 kV. All FD-MS spectra were recorded as a sum of stored spectra.

Results and Discussion

Figures 1 and 2 show FD-MS spectra in the m/z region 250—800 for normal and deuterated styrene oligomers synthesized in ethylbenzene, respectively. It is seen from Fig. 1 that four series of molecular ion-peak patterns are distinguished by each mass number "104", which is the repetitive unit interval of a normal styrene. These series of peaks are at $92+104n$ (m/z 300—404—508—612), $208+104n$ (m/z 312—416—520—624), $106+104n$ (m/z 314—418—522—626), and $222+104n$ (m/z 326—430—534—638), where n is an integer corresponding to the degree of polymerization. Then, they are generally formulated as "$K+104n$," where K is a constant and is equivalent to the sum of both the mass numbers of the head and tail end groups. In the case of deuterated styrene, five series are also expressed in the same way as normal styrene oligomers except for the repetitive unit interval "107" being applicable to deuterated styrene; the five series are at $94+107n$ (m/z 308—415—522—629), $106+107n$ (m/z 320—427—534—641), $210+107n$ (m/z 317—424—531—638), $214+107n$ (m/z 321—428—535—642), and $226+107n$ (m/z 333—440—547—654). They are generally formulated as "$K+107n$."

Figures 3 and 4 show FD-MS spectra in the m/z region 400—500 for normal and deuterated styrene oligomers synthesized in toluene, ethylbenzene, propylbenzene, and isopropylbenzene. Each oligomer peak in Figs. 3 and 4 is also classified in the above-mentioned way. These results are summarized in Tables 1 and 2 for normal and deuterated styrenes, respec-

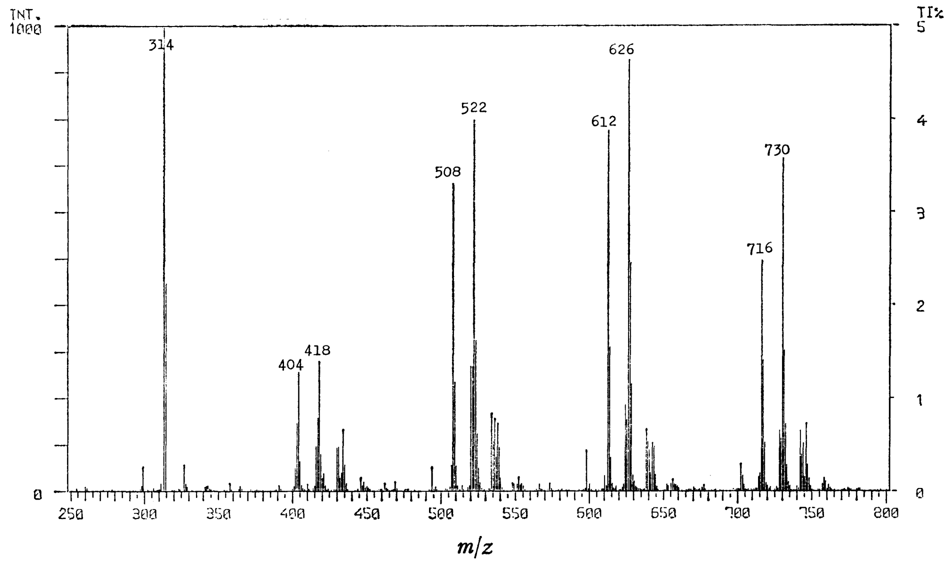


Fig. 1. FD-MS spectrum of normal styrene oligomers synthesized in ethylbenzene.

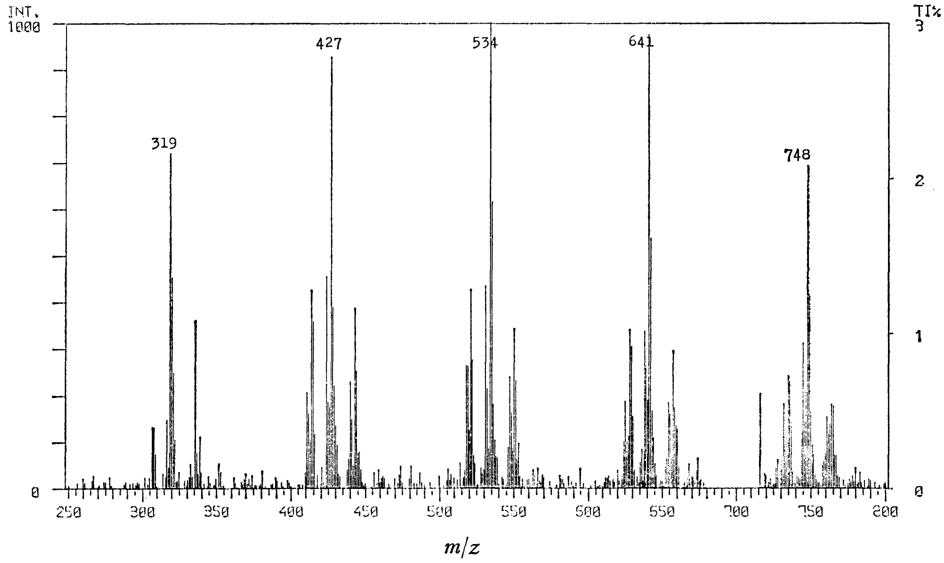


Fig. 2. FD-MS spectrum of deuterated styrene oligomers synthesized in ethylbenzene.

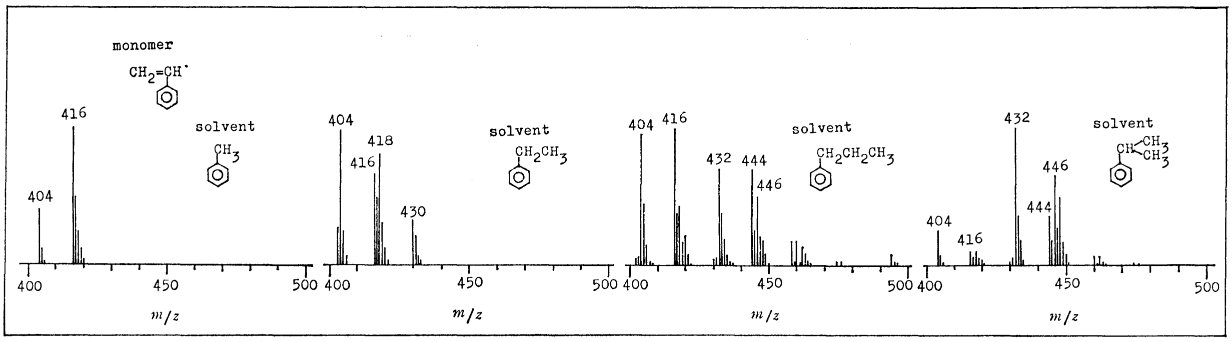
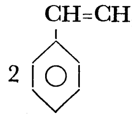


Fig. 3. FD-MS spectra (*m*/*z*; 400—500) of normal styrene oligomers synthesized in various solvents.

tively.

According to the reasonable proposal on the initiation mechanism for the thermal polymerization of styrene by Mayo[9] and Kopecky and Evani,[6] the first step is the Diels-Alder dimerization to form styrene dimers (SD) according to



$$2\,C_6H_5CH{=}CH_2 \longrightarrow SD^*\,. \qquad (1)$$

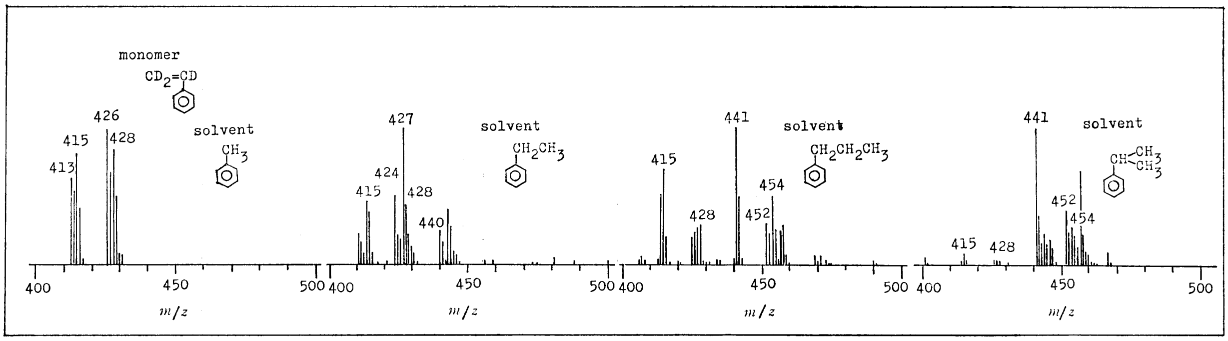


Fig. 4. FD-MS spectra (m/z; 400—500) of deuterated styrene oligomers synthesized in various solvents.

TABLE 1. MASS NUMBERS OF THE SPECIES DERIVED FROM THE PROPOSED MECHANISM FOR NORMAL STYRENE OLIGOMERS

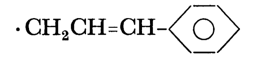
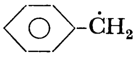
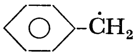
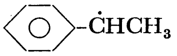
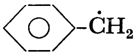
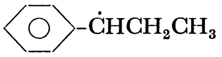
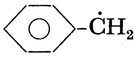
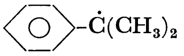
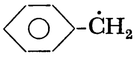
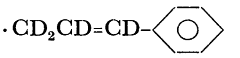
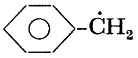
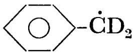
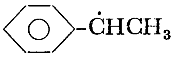
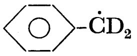
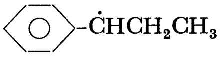
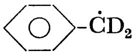
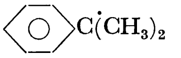
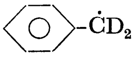
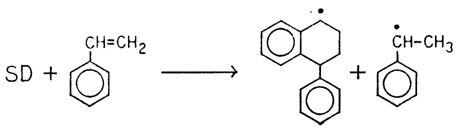
Solvent	Head group		Tail group			
			·H	1	 $\cdot CH_2CH{=}CH-$	117
Toluene	 $-\dot{C}H_2$	91	$92+(104)_n$		$208+(104)_n$	
	 $-\dot{C}H_2$	91	$92+(104)_n$		$208+(104)_n$	
Ethylbenzene	 $-\dot{C}HCH_3$	105	$106+(104)_n$		$222+(104)_n$	
	 $-\dot{C}H_2$	91	$92+(104)_n$		$208+(104)_n$	
Propylbenzene	 $-\dot{C}HCH_2CH_3$	119	$120+(104)_n$		$236+(104)_n$	
	 $-\dot{C}H_2$	91	$92+(104)_n$		$208+(104)_n$	
Isopropylbenzene	 $-\dot{C}(CH_3)_2$	119	$120+(104)_n$		$236+(104)_n$	
	 $-\dot{C}H_2$	91	$92+(104)_n$		$208+(104)_n$	

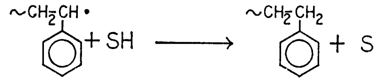
TABLE 2. MASS NUMBERS OF THE SPECIES DERIVED FROM THE PROPOSED MECHANISM FOR DEUTERATED STYRENE OLIGOMERS

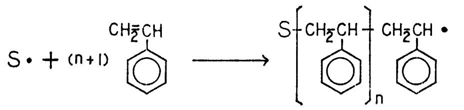
Solvent	Head group		Tail group			
			·H	1	 $\cdot CD_2CD{=}CD-$	121
Toluene	 $-\dot{C}H_2$	91	$92+(107)_n$		$212+(107)_n$	
	 $-\dot{C}D_2$	93	$94+(107)_n$		$214+(107)_n$	
Ethylbenzene	 $-\dot{C}HCH_3$	105	$106+(107)_n$		$226+(107)_n$	
	 $-\dot{C}D_2$	93	$94+(107)_n$		$214+(107)_n$	
Propylbenzene	 $-\dot{C}HCH_2CH_3$	119	$120+(107)_n$		$240+(107)_n$	
	 $-\dot{C}D_2$	93	$94+(107)_n$		$214+(107)_n$	
Isopropylbenzene	 $\dot{C}(CH_3)_2$	119	$120+(107)_n$		$240+(107)_n$	
	 $-\dot{C}D_2$	93	$94+(107)_n$		$214+(107)_n$	

In a subsequent step, SD reacts with a third styrene monomer in a molecule-induced homolysis to produce two kinds of radicals according to

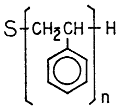

(2)

These two radicals then initiate polymerization, and under our experimental conditions employing circumstances with much more solvent, it is expected that the propagation radicals stimulate the chain transfer to solvent molecules (SH) and furthermore that solvent radicals with hydrogen atom abstracted should play a major role as a reinitiator according to


(3)


(4)

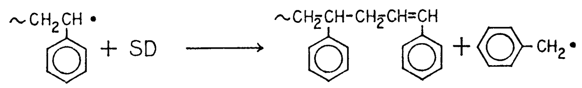
On the basis of the dependency of reactivity on the kind of solvents, the mass numbers of normal styrene oligomers with *K*'s 92, 106, and 120 in Table 1 are assigned to the molecular species

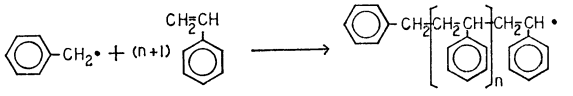

(5)

It is shown in Table 2 that such series as have the same *K*'s are observed in deuterated styrene oligomers as well. On the contrary, existence of such molecular species as are independent of the kind of solvents is indicated which have *K*'s 92 and 208 for normal styrene oligomers and 94 and 214 for deuterated ones in Tables 1 and 2, respectively.

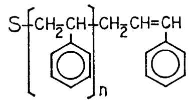
Though with no detailed discussion on the mechanism of the chain transfer, Pryor and Coco[10] pointed out from a computer simulation that the propagation mechanism for the thermal polymerization of styrene should be related to the chain transfer of SD and that at 60 °C the chain transfer constant, Cm*, for SD was 10^2—10^3 times higher than that for any aromatic hydrocarbon solvents used here. In our present investigation, the chain transfer to the solvent could occur with a rather high probability because of the low concentration of styrene monomer (below 1 mol%).

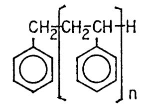
In order to explain the appearance of molecular species given in Tables 1 and 2, it is assumed that the chain transfer of propagating radicals to SD should follow the reaction sequences

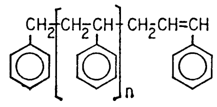

(6)

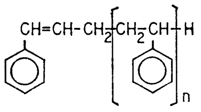

(7)

Thus, if the propagating radicals encounter SD, the SD makes a cleavage into benzyl and 3-phenyl-2-propenyl radicals, and then the 3-phenyl-2-propenyl radicals are combined with the propagating radicals, while the benzyl radicals only contribute to the reinitiation process. According to this assumption and considering the chain transfer to solvents, it may be expected that there should exist two head groups and two tail groups, and therefore that the four molecular species represented by Formula 5 and the following formulas should be observed in FD-MS spectra.


(8)


(9)


(10)


(11)

Indeed, our experimental results may support the proposed mechanism. Furthermore, it is clarified that the abstraction reaction of a benzyl group through the chain transfer to SD dose not occur, as evidenced by the fact that no such molecular species as shown by Formula 11 appears in any FD-MS spectra.

In Figs. 3 and 4, besides the peaks attributed to the chemical structures for Formulas 5 and 8—10, molecular ion peaks independent of the kind of solvents, whose *K*'s correspond to 182, 210, and 238, are observed. They are thought as being produced by the recombination termination between the propagating radicals, since there are generally two termination processes, that is, recombination and disproportionation, and moreover it was reported that the probability of the recombination termination for styrene is nearly 100%.[11] Other intense peaks in Figs. 1 and 2 are observed at 312 and 321 for normal and deuterated styrene oligomers, respectively. These peaks are assigned to the molecular species formed in the trimerization of monomers. These results are in agreement with the fact that the radical pair produced in the reaction between SD and styrene monomers should generate the cage reaction to form trimeric products concertedly against the chain initiation.[12]

In conclusion, it was proved from a detailed analysis of molecular ion peaks observed in FD-MS spectra that some kinds of reactions were generated in the styrene polymerization. They are radical telomerization to solvents and SD and recombination termination and cage reaction between initiating or propagating radicals. Thus, it has been found that the

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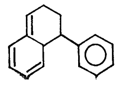
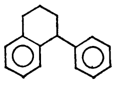
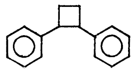
* SD may be considered as such intermediates:







FD-MS is effective for the investigation on the polymerization mechanism. However, it is not sufficient to discuss the quantitative analysis owing to the bad reproducibility of peak intensities. In near future, if high sensitive measurement in the high mass region becomes available, the whole polymerization mechanism might get clarified and confirmed more accurately.

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