Evidence for the Presence of Cage Reaction in the Initiation Step of Thermal Polymerization of Styrenes by Field Desorption Mass Spectrometry

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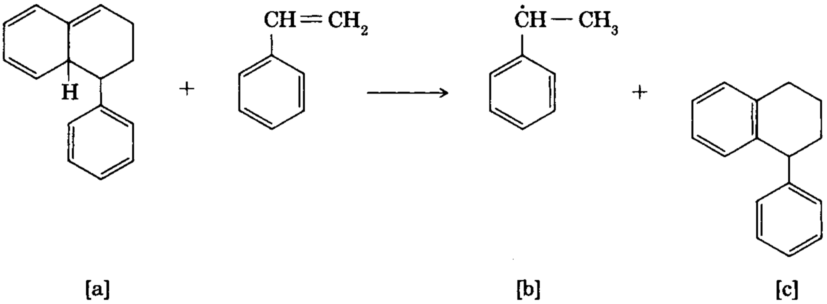
Synopsis

Field desorption mass spectrometry (FDMS) was applied to the study of the initiation mechanism of thermal polymerization of styrenes. The FD mass spectrum was measured for a cooligomer of α,β,β-trideuterostyrene and p-methoxystyrene produced by thermal polymerization using ethylbenzene as a solvent, and this was compared with the spectrum of an oligomer of p-methoxystyrene. The above two FD mass spectra showed characteristic differences, depending upon the number of hydrogen and deuterium atoms and upon the presence or absence of the methoxy group, in the oligomers. Molecular species observed in the spectra were identified based on these considerations. As a result, we could distinguish the "true trimer" produced from three monomers from the "cross trimer" produced from fragments of five monomers. It was found that the "true trimer" was the major constituent in the trimer region, and that the "true trimer" was produced mainly by the cage reaction between initiating radicals.

INTRODUCTION

For the spontaneous initiation mechanism of the thermal polymerization of styrenes, the scheme proposed by Mayo[1] has generally been accepted.[2,3] That is, styrene dimer[a] is produced by the Diels-Alder condensation of two styrene monomers as a first step. The styrene dimer then reacts with styrene monomer to form a 1-phenylethyl radical[b] and a 4-phenyltetralino radical[c], as shown in eq. (1). These radicals are believed to initiate polymerization.



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On the other hand, proposals which are in conflict with the above reaction scheme have been also reported.[4,5] Although the scheme proposed by Mayo involves a hydrogen atom transfer reaction between a Diels–Alder dimer and monomer molecules, Pryor and Huang[4] reported that the thermal polymerization of pentafluorostyrene had a rate which is similar to that of styrene, in spite of the difficulty of transferring a fluorine atom. In addition to this, the detection of the 4-phenyltetralino group as an end group of the polystyrene produced thermally has not been reported until now. Accordingly, the initiation mechanism of the thermal polymerization of styrenes has not yet been fully clarified and established.

In recent years, there has been a growing interest in field desorption mass spectrometry (FDMS) as a novel analytical tool for the characterization of polymers.[6–13] An advantage of FDMS is that it normally gives molecular ions as the strongest peaks without noticeable fragmentation.[6–9] The authors have reported the FD mass spectra of styrene oligomers synthesized thermally using aromatic hydrocarbons as solvents.[10–13] In these studies, the ion at m/z 312 was usually found to be the base peak. From this observation, we have suggested that a styrene trimer produced by the cage reaction may be formed as a major product. Though the production of a styrene trimer by the cage reaction was proposed by Brown,[5] the precise structure of the trimeric species has not been identified.

The styrene trimer produced by the cage reaction can be formed by the combination of two radicals produced in the initiation step of the thermal polymerization. Therefore, it is of interest to determine if the trimeric species of molecular weight 312 can be established as the product of a cage reaction. In order to do this, it is necessary that the molecular weight 312 species is shown to contain lesser amount of trimers produced by reactions other than the cage reaction.

In this study, we have measured and analyzed the FD mass spectrum of a cooligomer of α,β,β-trideuterostyrene and p-methoxystyrene in order to assign the ion peaks in the trimer range and to determine if the contribution of the cage reaction is dominant for the production of trimeric styrene.

EXPERIMENTAL

Materials. Ethylbenzene and p-methoxystyrene (PMS) were commercially obtained and were purified by distillation just before use. α,β,β-Trideuterostyrene (DS) with an enrichment of 98% was purchased from Merck Sharp and Dohme, Ltd., and was used without further purification.

The thermal polymerization was carried out by heating a sealed glass tube containing the monomer dissolved in ethylbenzene solvent at a weight ratio of 1/99. The monomer sample consisted of DS and PMS with the molar ratio of 1/1 or else PMS alone. As the first step, 2 mL of the sample was placed into the glass tube (12 mm i.d., 200 mm length). The tube was cooled to dry ice temperature, degassing *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, the solvent in the reaction tube was allowed to evaporate, and the remaining oligomers were dissolved in chloroform for FDMS analysis. We shall call the cooligomers of DS and PMS "oligomer DM," and the PMS oligomer "oligomer M."

Apparatus. FD mass spectra were measured on a JEOL Model JMS DX-300 Double Focusing Mass Spectrometer. The samples were loaded on a standard carbon emitter. Measurement conditions were as follows: The temperature of the ion source was 50°C. Mass spectral resolution ($M/\Delta M$) was 1000. The mass was scanned from 100 to 1000 amu in 10 s. Accelarating and cathode voltages were 3.0 kV and -5.5 kV, respectively. The emitter heating current was increased from 0 to 30 mA at the rate of 2 mA/min. Output signal from the mass spectrometer was processed by a JEOL JMA-3500 Data Processing System. Mass numbers were calibrated with perfluorokerosene and poly(perfluoropropylene oxide) in EI mode. All of the FD mass spectra reported in this study were obtained by summing the spectra acquired as the emitter heating current was gradually increased.

RESULTS AND DISCUSSION

The styrene homooligomers synthesized by thermal polymerization have been examined by FDMS previously.[12] The major oligomers can be classified into the following four groups:

$$\text{Sv–M}_n\text{–H [d]},\quad \text{Sv–M}_n\text{–Pr [e]},\quad \text{Bz–M}_n\text{–H [f]},\quad \text{Bz–M}_n\text{–Pr [g]}$$

where Sv, M, *n*, H, Pr, and Bz represent the phenylethyl group, the monomeric repeating unit, an integer corresponding to the degree of polymerization, a hydrogen atom, a phenylpropenyl group, and a benzyl group, respectively. There are several possible structures for the phenylpropenyl group, including $—CH_2—CH{=}CH—Ph$, $—CH(Ph)—CH{=}CH_2$, and $—CH_2—C(Ph){=}CH_2$, among others. The determination of the precise structure has not been carried out. In the FD mass spectra reported previously,[12] the initiating radicals could not be identified. This may be due to the fact that the rate constant of the chain transfer reaction is larger than that of the reaction producing initiating radicals. Thus, no information about the structures of the initiating radicals could be obtained.

From the fact that the molecular species produced can be classified into four groups, it may be surmised that a chain-transfer reaction as shown in eq. (2) is dominant in the thermal polymerization of styrenes:

$$\text{P}\cdot + \text{Sd} \rightarrow \text{P—Pr} + \text{Bz}\cdot \qquad (2)$$

where $\text{P}\cdot$ and Sd represent a polymer radical and the styrene dimer, respectively.

Based on the considerations mentioned above, thermal polymerization mechanism for the production of styrene oligomer can be expressed as follows:

$$\text{St} + \text{St} \rightarrow \text{Sd} \qquad (3)$$

$$\text{Sd} + \text{St} \rightarrow \text{R}_1\cdot + \text{R}_2\cdot \qquad (4)$$

$$\text{R}\cdot + n\text{M} \rightarrow \text{R–M}_n\cdot \qquad (5)$$

$$\text{R–M}_n\cdot + \text{Sv–H} \rightarrow \text{R–M}_n\text{–H} + \text{Sv}\cdot \qquad (6)$$

$$\text{R–M}_n\cdot + \text{Sd} \rightarrow \text{R–M}_n\text{–Pr} + \text{Bz}\cdot \tag{7}$$

$$\text{Sv}\cdot + n\text{M} \rightarrow \text{Sv–M}_n\cdot \tag{8}$$

$$\text{Sv–M}_n\cdot + \text{Sv–H} \rightarrow \text{Sv–M}_n\text{–H} + \text{Sv}\cdot \tag{9}$$

$$\text{Sv–M}_n\cdot + \text{Sd} \rightarrow \text{Sv–M}_n\text{–Pr} + \text{Bz}\cdot \tag{10}$$

$$\text{Bz}\cdot + n\text{M} \rightarrow \text{Bz–M}_n\cdot \tag{11}$$

$$\text{Bz–M}_n\cdot + \text{Sv–H} \rightarrow \text{Bz–M}_n\text{–H} + \text{Sv}\cdot \tag{12}$$

$$\text{Bz–M}_n\cdot + \text{Sd} \rightarrow \text{Bz–M}_n\text{–Pr} + \text{Bz}\cdot \tag{13}$$

where St and Sd represent styrene and styrene dimer, respectively. $R_1\cdot$ and $R_2\cdot$ represent the two initiating radicals produced by the reaction of styrene dimer with styrene, and $R\cdot$ represents both radicals of R_1 and of R_2.

In the case of styrene homooligomer, the molecular weight of the species Bz–M–Pr ($n = 1$ in [g]), produced by the reaction shown in eq. (13), is 312. On the other hand, molecular species produced by the cage reaction shown in eq. (14) can also give the same molecular weight. Accordingly, the origin of the intense ion at m/z 312 in the FD mass spectrum of styrene homopolymer can not be confirmed without isotopic labeling experiments. We shall call the species produced by eq. (13) "cross trimer" and the species produced by eq. (14) "true trimer":

$$R_1\cdot + R_2\cdot \rightarrow R_1\text{—}R_2 \tag{14}$$

Figure 1 shows the FD mass spectrum of oligomer M, that is, the oligomer of *p*-methoxystyrene (PMS). The molecular ions shown in Figure 1 can be subdivided into three oligomer types—trimers, tetramers, and pentamers. The trimer, tetramer, and pentamer ranges extend from m/z 340 to 430, from m/z 470 to 560, and from m/z 600 to 680, respectively. It can be seen from Figure 1 that the most intense ion in the trimer range is observed at m/z 402, which corresponds to PMS trimer. Other molecular ions are observed, in order of intensity, at m/z 390, 374, and 386. The major molecular ions in the tetramer region are observed, in order of intensity, at m/z 524, 508, 536, 520, 478, and 494. In the pentamer region, the major molecular ions are observed, in order of intensity, at m/z 658, 642, 670, 612, 654, and 628. It is also seen from Figure 1 that several series of peaks are present at constant repeating mass intervals which correspond to the molecular weight of the monomer. The major peaks observed in Figure 1 can be classified into several groups, and the classification is similar to the one reported previously.[12] The classification and the assignment of these peaks are summarized in Table I.

It was assumed in the above discussion and in the following discussion that the FD response factors for the oligomers used in this study are roughly equal. This is generally valid for hydrocarbon oligomers.[7,8] The contribution of ^{13}C isotope peaks was roughly taken into account in determining relative molecular ion abundances.

It can be seen from Figure 1 and Table I that the intensity of ion peaks

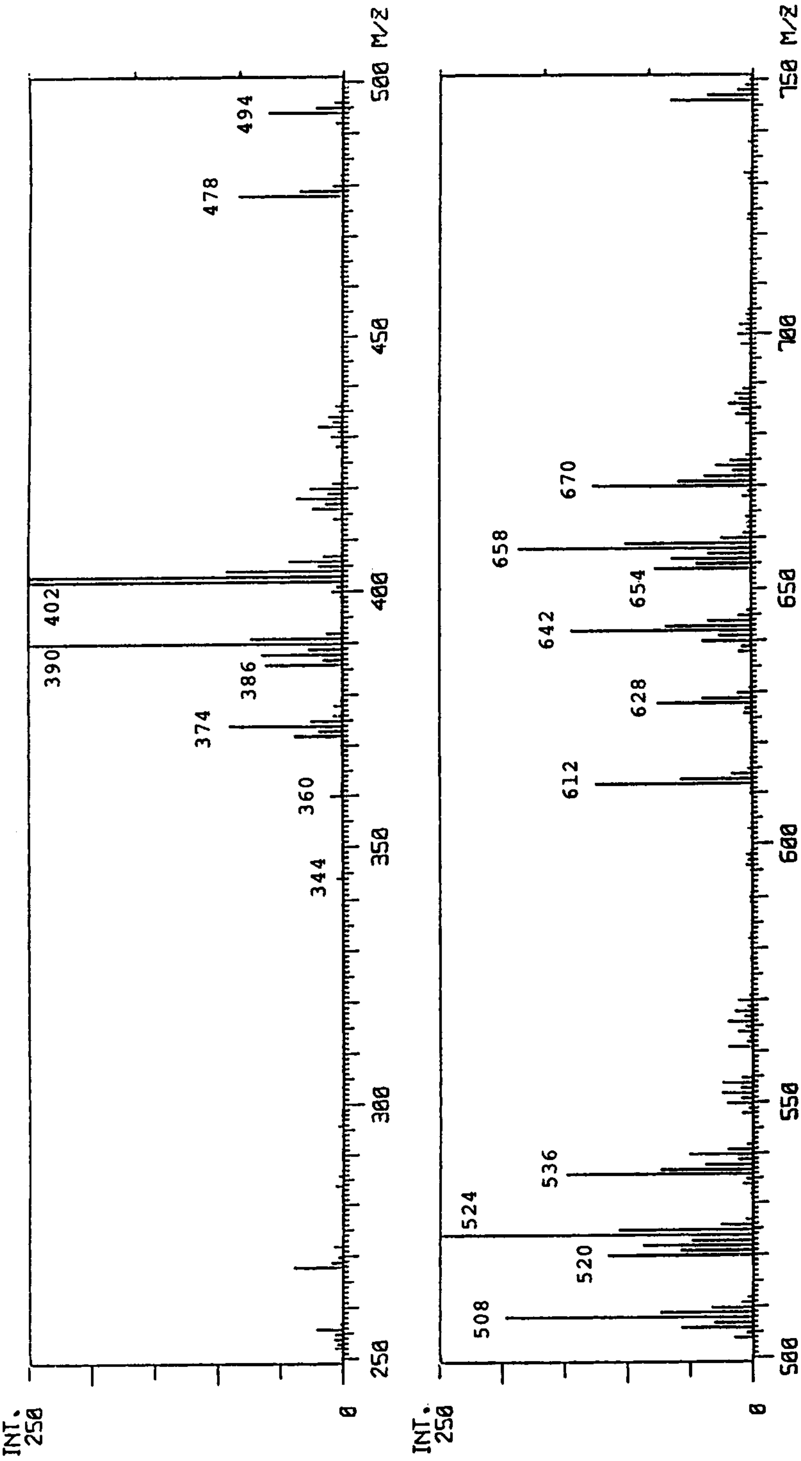


Fig. 1. FD mass spectrum of *p*-methoxystyrene oligomer synthesized by thermal polymerization.

TABLE I
Structures and Mass Numbers of Molecular Species for Oligomers of *p*-Methoxystyrene

Structure[a]		Trimers		Tetramers		Pentamers	
		n	m/z	n	m/z	n	m/z
Sv–M$_n$–H	[d]	2	374	3	508	4	642
Sv–M$_n$–Pr	[e]	1	386	2	520	3	654
Bz–M$_n$–H	[f]	2	390	3	524	4	658
Bz–M$_n$–Pr	[g]	1	402	2	536	3	670
Sv–M$_n$–Sv	[h]	1	344	2	478	3	612
Bz–M$_n$–Sv	[i]	1	360	2	494	3	628

[a] Sv, M, Bz, and Pr represent solvent residue, 1-phenylethyl group, monomeric unit (*p*-methoxystyrene), (*p*-methoxystyrene)methyl group, and (*p*-methoxyphenyl)propenyl group, respectively.

in the ranges of trimer, tetramer, and pentamer is, except for the ion at m/z 402 whose intensity is exceptionally large, generally found to be in the order of Bz–M$_n$–H [f], Sv–M$_n$–H [d], Bz–M$_n$–Pr [g], Sv–M$_n$–Pr [e], Sv–M$_n$–Sv [h], and Bz–M$_n$–Sv [i]. This observation is consistent with the previous results.[11,12] From these observations, the polymerization mechanism of PMS is believed to be similar to that of styrene, though the rate of the initiation reaction is somewhat larger than that of the chain-transfer reaction in the case of PMS. From the fact that the intensity of the peak at m/z 402 is exceptionally large, molecular species corresponding to m/z 402 result from a reaction whose mechanism is different from the reaction producing the other molecular species. Thus, we have considered the possibility of a cage reaction in the initiation step of the thermal polymerization. In order to determine if the origin of the trimeric species is a cage reaction, the following further work was carried out.

Figure 2 shows the FDMS spectrum of the oligomer DM, that is the cooligomer of α,β,β-trideuterostyrene (DS) and PMS. It is seen from Figure 2 that the major peaks can be classified into four groups, [d]–[g]. The classification is same as for the styrene or PMS oligomers. Accordingly, it can be postulated that the reaction mechanism for oligomer DM is similar to the one for styrene or PMS oligomers. In the case of oligomer DM, however, the monomeric unit M in the structures [d]–[g] can be either DS or PMS. Analogously, Pr can be the phenylpropenyl group or the (*p*-methoxyphenyl)propenyl group (Prm), and Bz can be the benzyl group or the (*p*-methoxyphenyl)methyl group (Bzm). Two kinds of structures are possible for Bz, Bzm, Pr, and Prm groups, and the difference between the two structures is due to the numbers of hydrogen and deuterium atoms that are present. The possible structures are summarized in Table II.

If we consider a styrene dimer having a structure analogous to that of [a] in eq. (1), there can be four styrene dimers in the case of the production of oligomer DM. The chain transfer reaction between the styrene dimers and a polymer radical can be expressed as the following equations, in the copolymerization of DS and PMS. These reactions can explain the formation of the oligomers listed in Table II:

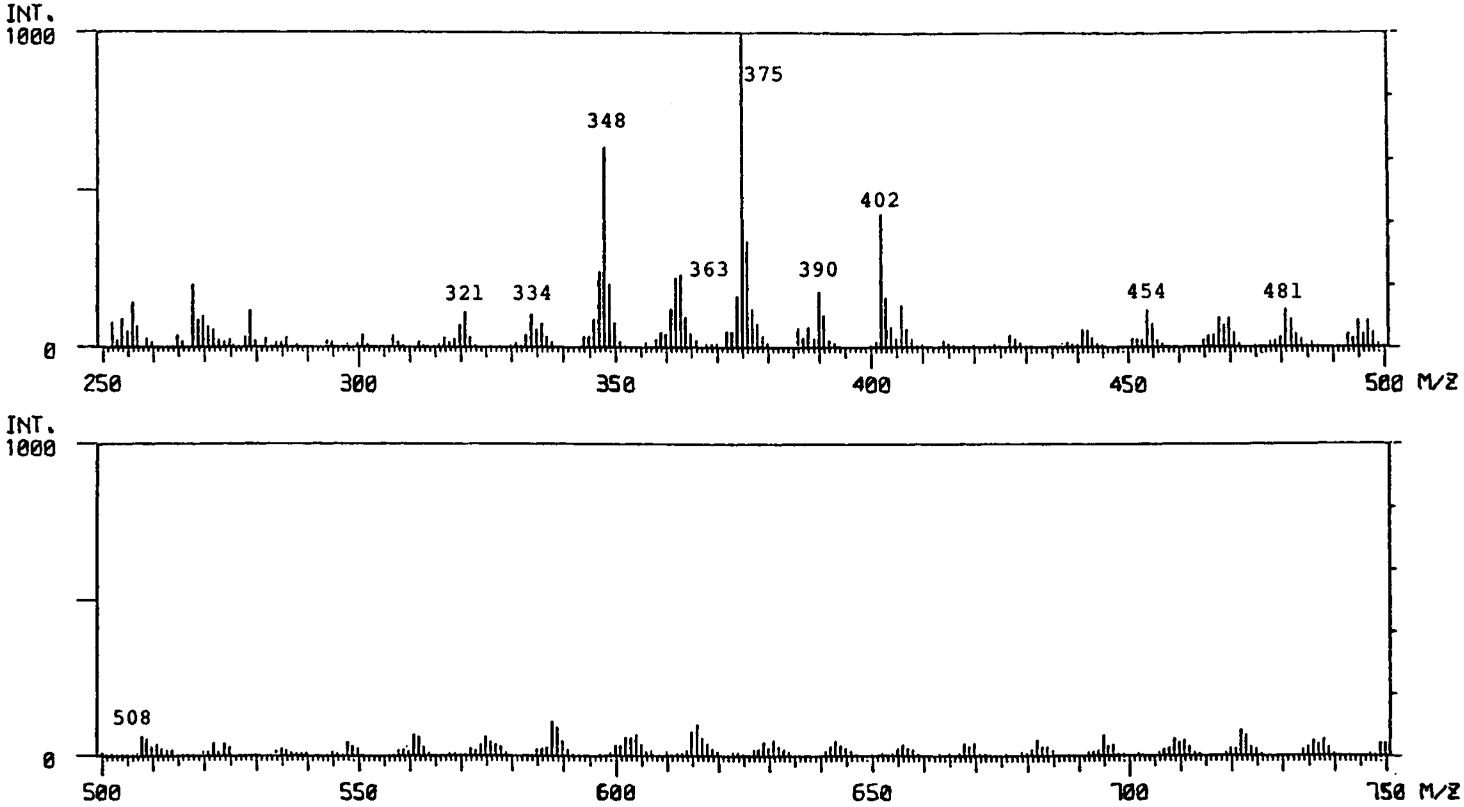
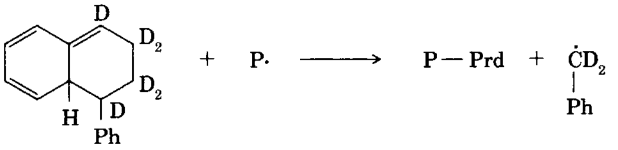


Fig. 2. FD mass spectrum of cooligomer of α,β,β-trideuterostyrene and p-methoxystyrene synthesized by thermal polymerization.

TABLE II
Structures and Molecular Weights of Constituent Groups

Group	Structure[a]	MW	Abbr.	Structure[a]	MW	Abbr.
Bz	$\begin{array}{l}CD_2\\ \vert \\ Ph\end{array}$	93	Bzd	$\begin{array}{l}CHD\\ \vert \\ Ph\end{array}$	92	Bzh
Bzm	$\begin{array}{l}CH_2\\ \vert \\ Phm\end{array}$	121	Bmh	$\begin{array}{l}CHD\\ \vert \\ Phm\end{array}$	122	Bmd
Pr	$\begin{array}{l}C_3D_4\\ \vert \\ Ph\end{array}$	121	Prd	$\begin{array}{l}C_3H_2D_2\\ \vert \\ Ph\end{array}$	119	Prh
Prm	$\begin{array}{l}C_3H_4\\ \vert \\ Phm\end{array}$	147	Pmh	$\begin{array}{l}C_3H_2D_2\\ \vert \\ Phm\end{array}$	149	Pmd

[a] Ph and Phm represents phenyl and 4-methoxyphenyl groups, respectively.



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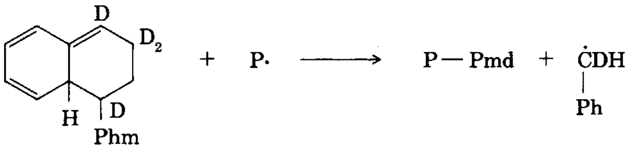

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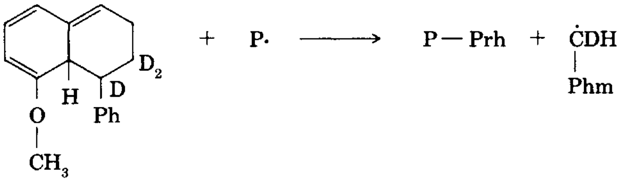

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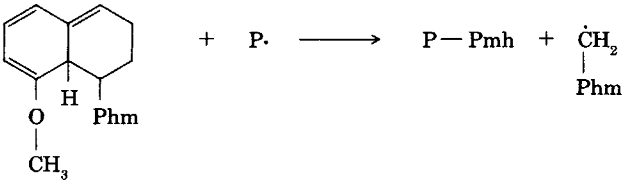

(18)

As can be seen from eq. (15), the Bz group is composed of the PhCH group of a monomer and an H atom of another monomer. On the other hand, the Pr group is composed of a Ph–C_2H_2 group of a monomer and a CH_2 group of another monomer. Thus, the "cross trimer" is formed by the combination of fragments from five monomers. However, the "true trimer" produced by the cage reaction is produced from three monomer molecules; that is, it is produced by the recombination termination reaction of two initiating radicals which are produced by the reaction of a styrene dimer with another styrene monomer.

Only one kind of structure exists for the molecules of Bz–M_n–Pr in case of styrene oligomers. However, many structures are possible in case of oligomer DM. For example, if the degree of polymerization is 2, four possible structures should be taken into account for each Bz and Pr group as listed in Table II. As for the monomer unit M, there are three possibilities for the combination of DS and PMS. That is, M can exist as DS/PMS = 2/0, 1/1, and 0/2. Accordingly, 48 structure types can be written. Since some of these species have the same molecular weight, only 27 species having different molecular weights can be distinguished by FDMS. For the oligomers of DM, the "true trimer" can be distinguished from the "cross trimer," since their molecular weights are different. Assignments of the major mass peaks observed in Figure 2 are summarized in Tables III and IV.

It is apparent from eq. (15) that Prd and Bzd groups form a pair. It is also seen from eqs. (16)–(18) that Pmd and Bzh, Prh and Bmd, and Pmh and Bmh also form pairs. Accordingly, the produced amount of the two groups making a pair should be same.

In order to eliminate the influence of the "true trimer" whose originating mechanism is different from that of the other molecular species, the amount of each pair of Bz and Pr groups was estimated by examining the FDMS spectrum shown in Figure 2 and Table IV.

Considering the molecular species of Bz–DM–H in Table IV, for example, it is seen from Figure 2 that the ions at *m/z* 363 and 334 corresponding to Bmh and Bzh groups, respectively, are observed with much larger intensity compared to the ions at *m/z* 364 and 335 corresponding to Bmd and Bzd groups. Considering the molecular species of Sv–M–Pr, Pmh and Pmd groups show larger ions at *m/z* 386 and 388, respectively, compared to the Prh and Prd groups with ions at *m/z* 358 and 360. From these results, the order of the amount of each pair can be described by the following relation:

$$\text{Bmh/Pmh} = \text{Bzh/Pmd} > \text{Bmd/Prh} = \text{Bzd/Prd}$$

This relation is also maintained for the higher mass oligomers. Based on these facts, the rate constants for the reaction designated by eqs. (15)–(18) are postulated to be in the order of (18) = (16) > (17) = (15).

In order to identify the "true trimer," the ion intensities in Figure 2 were examined in the trimer region. It is immediately seen from Figure 2 that the intensities of the ions at *m/z* 348, 375, and 402 are large compared to the others. These peaks as well as the one at *m/z* 321 correspond to trimeric species. That is, peaks at *m/z* 321, 348, 375, and 402 correspond to species having the composition; DS/PMS = 3/0, 2/1, 1/2, and 0/3, respectively. These exceptionally intense ions suggest the presence of another reaction mechanism in addition to the reactions shown in eqs. (3)–(13). It is concluded by comparing the ion intensities in the trimer range with those in the tetramer range that most of the molecular species at *m/z* 321, 348, 375, and 402 are "true trimers" produced by the cage reaction.

The following considerations also support the conclusion that the contribution of the cage reaction to the production of the trimeric species is large. By taking pairs of Bmh–M_2–Pmh (*m/z* 536) and Sv–M_2–Pmh (*m/z* 520) and of Bmh–M–Pmh (*m/z* 402) and Sv–M–Pmh (*m/z* 386), for example,

TABLE III

Structural Assignments for Tetramers (MWs 410–540)

Head group (MW)		Tail group (MW)[a]									
		H	(1)	Prh	(119)	Prd	(121)	Pmh	(147)	Pmd	(149)
Sv	(105)	D3	427	D2	438	D2	440*	D2	466	D2	468
		D2M	454	DM	465	DM	467	DM	493	DM	495
		DM2	481	M2	492*	M2	494	M2	520	M2	522
		M3	508								
Bzh	(92)	D3	414	D2	425*	D2	427	D2	453	D2	455
		D2M	441	DM	452	DM	454	DM	480	DM	482
		DM2	468	M2	479	M2	481	M2	507*	M2	509
		M3	495								
Bzd	(93)	D3	415*	D2	426*	D2	428	D2	454	D2	456
		D2M	442	DM	453	DM	455	DM	481	DM	483
		DM2	469	M2	480	M2	482	M2	508	M2	510
		M3	496								
Bmh	(121)	D3	443	D2	454	D2	456#	D2	482	D2	484
		D2M	470	DM	481	DM	483#	DM	509	DM	511
		DM2	497	M2	508	M2	510	M2	536	M2	538*
		M3	524								
Bmd	(122)	D3	444#	D2	455	D2	457#	D2	483	D2	485*
		D2M	471	DM	482	DM	484	DM	510	DM	512
		DM2	498	M2	509	M2	511	M2	537*	M2	539*
		M3	525								

[a] D and M represent α,β,β-trideuterostyrene (DS) and *p*-methoxystyrene (PMS), respectively. For example, DM2 represents an oligomer composed of one DS and of two PMS. Mass numbers designated by * and by # represent species that are low in abundance and species obscured because of the C-13 natural abundance, respectively.

TABLE IV
Structural Assignments for Trimers (MWs 300–410)

Head group		Tail group (MW)[a]									
	(MW)	H	(1)	Prh	(119)	Prd	(121)	Pmh	(147)	Pmd	(149)
Sv	(105)	D2	320	D	331*√	D	333	D	359	D	361
		DM	347	M	358	M	360	M	386	M	388
		M2	374								
Bzh	(92)	D2	307	D	318#	D	320	D	346	D	348
		DM	334	M	345	M	347	M	373	M	375
		M2	361								
Bzd	(93)	D2	308	D	319	D	321	D	347	D	349
		DM	335	M	346	M	348	M	374	M	376#
		M2	362								
Bmh	(121)	D2	336	D	347	D	349	D	375	D	377
		DM	363	M	374	M	376#	M	402	M	404
		M2	390								
Bmd	(122)	D2	337	D	348	D	350	D	376#	D	378
		DM	364	M	375	M	377	M	403	M	405
		M2	391								

[a] Notations are the same as in the Table III.

ratios of the intensity of the corresponding ion peaks are estimated as follows:

$$\text{Bmh–M}_2\text{–Pmh/Sv–M}_2\text{–Pmh} = 1.3/1, \quad \text{Bmh–M–Pmh/Sv–M–Pmh} = 6.7/1$$

From the fact that the ratio of the intensity of the latter pair is larger than that of the former pair, it can be said that the species of molecular weight 402 is mainly produced by the cage reaction, and that the contribution of the reaction shown in eq. (13) to the production of the trimeric species is very small.

From the above discussions, it can be concluded that the styrene trimer at *m/z* 312 is the "true trimer" produced by the cage reaction and that the contribution of the "cross trimer" to *m/z* 312 is very small.

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