Macromolecules

Volume 14, Number 3 May–June 1981

Cationic Oligomerization of Unsaturated Dimers of Styrene and *p*-Methylstyrene

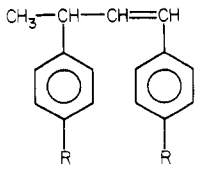
Mitsuo Sawamoto and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received January 17, 1980*

ABSTRACT: The reactions of the unsaturated dimers of styrene and *p*-methylstyrene with CF_3SO_3H or CH_3COClO_4 yielded trimers and tetramers as the major products in 1,2-dichloroethane at 50 or 70 °C; $BF_3O(C_2H_5)_2$ was inactive as a catalyst for the styrene dimer. The formation of the trimers from the dimers revealed the depolymerization of the intermediate dimer cations, which has been disregarded in the polymerization of the styrenes. ^1H and ^{13}C NMR structural analysis showed that the trimer fraction consists mainly of a cyclic isomer (the structure was determined) together with minor unsaturated isomers. The major part of the tetramers had cyclic end groups and the tetramer content increased (maximum ca. 60 wt %) at a lower dimer concentration and in a more polar solvent. A reaction pathway involving the depolymerization process is proposed.

A series of studies on cationic oligomerizations reported from our laboratories have recently provided an efficient, selective method for the dimerization of styrene[1-3] and its derivatives.[4,5] Thus, for example, the unsaturated linear dimers of styrene and *p*-methylstyrene (pMeSt) were prepared highly selectively (≥90%) with oxo acid catalysts such as trifluoromethanesulfonic acid (CF_3SO_3H) and acetyl perchlorate (CH_3COClO_4).

The potential polymerizability of dimers **1** and **2** with



1, R = CH_3
2, R = H

an acidic catalyst has drawn our attention because they may give products that considerably differ in structure and molecular weight distribution (MWD) from the oligomers obtained directly from styrene or pMeSt. The simplest product may be a branched tetramer, the synthesis of which is not available in the literature.

The acid-catalyzed reactions of the styrene dimer (**2**) and related compounds were studied by several workers[6-9] because of their relevance to the cationic dimerization and polymerization of styrene. To account for the product composition in the dimerization of styrene in aqueous sulfuric acid, Rosen[6] suggested the protonation of **2** followed by cyclization and/or addition to styrene or **2** itself. Barton and Pepper[8] kinetically investigated the conversion of the unsaturated dimers of styrene and α-methylstyrene into their cyclic isomers (e.g., 1-methyl-3-phenylindan for **2**) catalyzed by protonic acids. A spectroscopic analysis on the same systems by Bertoli and Plesch[9] showed the formation of cyclic cations from the unsaturated dimers. Although these papers briefly describe the polymerization of the dimers, concurrent with their cyclization, the structure and MWD of the products have not been analyzed. The cyclization of the linear dimer of 1,1-diphenylethene was studied in detail by Evans and coworkers.[10-12]

The present study deals with the acid-catalyzed oligomerization of unsaturated dimers **1** and **2**, with emphasis on the structure and MWD of products. Trimers and tetramers of styrene or pMeSt were obtained in good yields under specific conditions. Characterization of the products led to the formulation of a new reaction pathway involving the depolymerization (fragmentation) of the dimer cations.

Experimental Section

Materials. Commercial styrene and pMeSt were freshly distilled twice over calcium hydride under reduced pressure. Dimers **1** and **2** were prepared by the selective dimerization of the corresponding monomers with CH_3COClO_4 in benzene at 50 °C.[2,4] Fractionation of the crude products by preparative gel permeation chromatography (GPC) gave the linear dimers with purities better than 99%. Commercial CF_3SO_3H (Sumitomo 3M, purity ≥98%) was used as reported.[11] CH_3COClO_4 was prepared from acetyl chloride and silver perchlorate.[12] Boron trifluoride etherate ($BF_3O(C_2H_5)_2$) was used after distillation of the commercial product. 1,2-Dichloroethane ($(CH_2Cl)_2$) was washed with 10% aqueous sodium hydroxide solution and then water, was dried overnight with calcium chloride, and was distilled successively over phosphorus pentoxide and calcium hydride before use. Benzene (C_6H_6) and nitrobenzene ($C_6H_5NO_2$) were washed successively with concentrated sulfuric acid, water, 10% sodium

0024-9297/81/2214-0467$01.25/0

Table I
Cationic Oligomerization of Styrene Dimer (2) at 50 °C[a]

no.	catalyst	solvent	$[2]_0$, M	conv,[b] %	product composition,[c] wt % $n=3$	$n=4$	$n=5$	$n=6$	$n\geq 7$	$n=(3+4)$[d]
1	CF_3SO_3H	$(CH_2Cl)_2$	0.050	75	23	61	7.9	7.1	1.4	(84)
2	CF_3SO_3H	$(CH_2Cl)_2$	0.10	83	16	59	9.4	12	2.9	(75)
3[e]	CF_3SO_3H	$(CH_2Cl)_2$	0.10	78	22	56	9.8	9.4	2.7	(78)
4	CF_3SO_3H	C_6H_6	0.10	83	30	35	8.1	18	9.0	(65)
5	CF_3SO_3H	$(CH_2Cl)_2/C_6H_5NO_2$[f]	0.10	80	19	52	9.5	16	3.7	(71)
6	CH_3COClO_4	$(CH_2Cl)_2$	0.10	86	18	52	9.7	15	5.6	(70)
7	$BF_3O(C_2H_5)_2$	$(CH_2Cl)_2$	0.10	0						

[a] $[C]_0$ = 10 mM; reaction time, 10 min. [b] Conversion of the dimer 2 to higher oligomers (by GPC); its loss by cyclization is not included. [c] Determined by GPC; n denotes the degree of polymerization. [d] Total amount of trimers and tetramers. [e] At 70 °C. [f] $[C_6H_5NO_2]$ = 50 vol %.

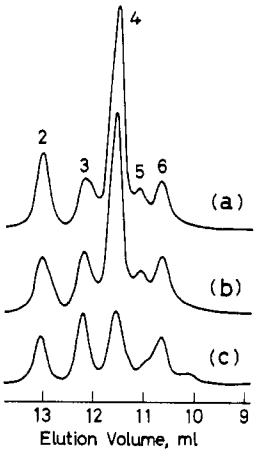


Figure 1. Product distributions in the oligomerization of styrene dimer (2) at 50 °C (samples 2, 4, and 6, Table I): $[2]_0$ = 0.10 M; $[C]_0$ = 10 mM. Catalyst and solvent: (a) CF_3SO_3H, $(CH_2Cl)_2$; (b) CH_3COClO_4, $(CH_2Cl)_2$; (c) CF_3SO_3H, C_6H_6. Numbers indicate the degree of polymerization.

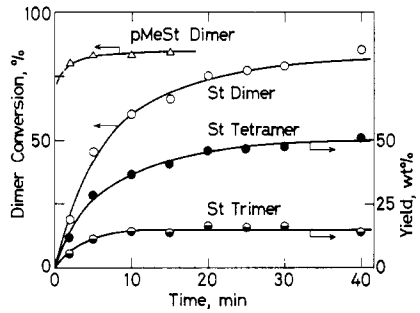


Figure 2. Time course of the oligomerizations of styrene dimer (2) and pMeSt dimer (1) by CF_3SO_3H in $(CH_2Cl)_2$ at 50 °C: $[1]_0 = [2]_0$ = 0.10 M; $[C]_0$ = 2.0 mM; yield based on 2.

hydroxide solution, and water, were dried overnight with calcium chloride, and finally were distilled over calcium hydride at least twice prior to use.

Procedures. Oligomerization of the dimers was performed under dry nitrogen at 50 or 70 °C. Reactions were initiated by addition of a catalyst solution to a dimer solution. After quenching with ammoniacal methanol, the reaction mixture was washed with distilled water to remove the catalyst residue. The products were then recovered by evaporating the organic layer to dryness and were vacuum dried.

The MWD of oligomers was measured by GPC in chloroform on a Jasco TRI-ROTAR chromatograph equipped with a polystyrene gel column (JSP 101; 21.5-mm i.d. × 500 mm; 2×10^4 theoretical plates/500 mm; exclusion limit $<3 \times 10^3$). Fractionation of the products was done by preparative, recycling GPC on the same apparatus and column. ^1H NMR (100-MHz) spectra were recorded in carbon tetrachloride at 31 °C on a Varian HA 100-D spectrometer. ^{13}C NMR (22.50 MHz) and ^1H NMR (90 MHz) spectra were obtained in $CDCl_3$ at room temperature on a JEOL FX-90Q spectrometer.

Results and Discussion

Oligomerization of Styrene Dimer. Styrene dimer (2) was treated with CF_3SO_3H, CH_3COClO_4, or $BF_3O(C_2H_5)_2$ catalyst. Table I summarizes the yield and the composition of the products obtained under a variety of reaction conditions. Typical MWD curves are shown in Figure 1.

With CF_3SO_3H dimer 2 was readily oligomerized to high conversion in $(CH_2Cl)_2$ at 50 °C to give colorless semisolids containing ca. 60 wt % styrene tetramers (Figure 1a). The higher oligomers were considerably reduced at a lower concentration of 2 (no. 1, Table I), where the total content of trimers and tetramers amounted to 84 wt %. Reactions in a more polar solvent (no. 5) or at a higher temperature (no. 3) also gave products having high tetramer contents. A nonpolar solvent (C_6H_6), however, resulted in a different material with a broad MWD (Figure 1c).

Table II
Dependence of Product Composition on Conversion in the Oligomerization of Styrene Dimer (2) by CF_3SO_3H in $(CH_2Cl)_2$ at 50 °C[a]

no.	time, min	conv,[b] %	product composition,[c] wt % $n=3$	$n=4$	$n=5$	$n=6$	$n\geq 7$	$n=(3+4)$[d]
1	2	19	29	61	5.5	4.2	0	(90)
2	5	46	25	63	5.3	7.2	0	(88)
3	10	61	24	60	7.1	8.5	0.6	(84)
4	25	77	21	60	8.0	10	0.8	(81)
5	40	85	16	60	9.3	12	2.5	(76)

[a] $[2]_0$ = 0.10 M; $[C]_0$ = 2.0 mM. [b] Conversion of the dimer 2 to higher oligomers (by GPC); its loss by cyclization is not included. [c] Determined by GPC; n denotes the degree of polymerization. [d] Total amount of trimers and tetramers.

Analogous experiments with CH_3COClO_4 as catalyst yielded similar products. An example is given in Table I (no. 6) and Figure 1b. On the other hand, $BF_3O(C_2H_5)_2$ was inactive as a catalyst; dimer 2 was recovered quantitatively from the reaction mixture without cyclization (no. 7). Thus, the styrene dimer (2) can be effectively converted to higher oligomers by oxo acid catalysts (CF_3SO_3H and CH_3COClO_4), the major products being tetramers and trimers.

It is worth noting that the reactions of the dimer led to considerable amounts of trimers and pentamers. The mechanistic implication of this fact will be discussed later.

Figure 2 illustrates the time course of the oligomerization of 2 by CF_3SO_3H in $(CH_2Cl)_2$. Table II shows the changes in product composition with dimer conversion. The con-

Table III
Cationic Oligomerization of *p*-Methylstyrene Dimer (1)[a]

no.	catalyst	solvent	temp, °C	$[1]_0$, M	conv,[b] %	product composition,[c] wt %				
						$n = 3$	$n = 4$	$n = 5$	$n \geq 6$	$n = (3 + 4)$[d]
1	CF_3SO_3H	C_6H_6	50	0.10	79	27	50	14	10	(77)
2	CF_3SO_3H	$(CH_2Cl)_2$	50	0.10	81	31	55	10	4.0	(86)
3	CF_3SO_3H	$(CH_2Cl)_2$	50	0.050	74	34	56	8.2	2.1	(90)
4	CF_3SO_3H	$(CH_2Cl)_2$	70	0.10	72	36	53	8.3	3.1	(89)
5	$BF_3O(C_2H_5)_2$	C_6H_6	50	0.10	20	32	49	12	7.2	(81)
6	$BF_3O(C_2H_5)_2$	$(CH_2Cl)_2$	50	0.10	27	33	52	10	5.4	(85)
7	$BF_3O(C_2H_5)_2$	$(CH_2Cl)_2$	70	0.10	24	40	49	6.9	4.0	(89)

[a] $[C]_0$ = 10 mM; reaction time, 10 min. [b] Conversion of the dimer 1 to higher oligomers (by GPC); its loss by cyclization is not included. [c] Determined by GPC; n denotes the degree of polymerization. [d] Total amount of trimers and tetramers.

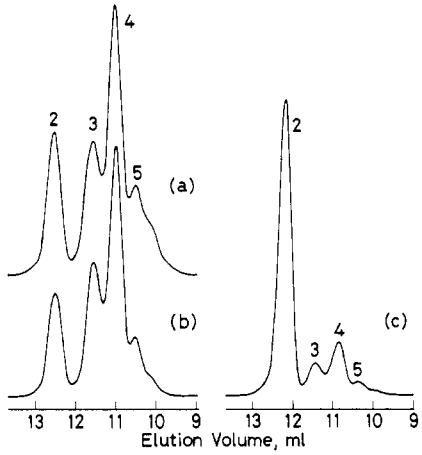


Figure 3. Product distributions in the oligomerization of pMeSt dimer (1) at 50 °C (samples 1, 2, and 6, Table III): $[1]_0$ = 0.10 M; $[C]_0$ = 10 mM. Catalyst and solvent: (a) CF_3SO_3H, C_6H_6; (b) CF_3SO_3H, $(CH_2Cl)_2$; (c) $BF_3O(C_2H_5)_2$, $(CH_2Cl)_2$. Numbers indicate the degree of polymerization.

version of **2** to higher oligomers reached ca. 80% in 20 min and apparently stopped at this stage. This is caused by the isomerization of **2** to the nonpolymerizable cyclic dimer (1-methyl-3-phenylindan; **2C**) as demonstrated below.

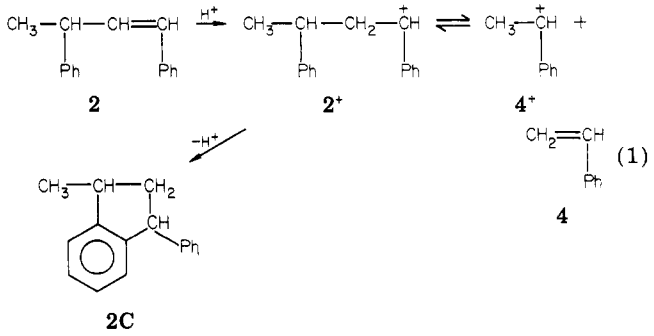
The product at the lowest conversion had the highest total content of trimers and tetramers (90 wt %). The tetramers increased with increasing conversion, but the yield of the trimers clearly leveled off in the early stages of reaction, resulting in a progressive decrease in their relative content in the product. These results indicate that the trimers, once formed, further react to yield higher oligomers that appeared only at a high conversion (Table II). The secondary reaction of the trimers was also shown by structural analysis by ^1H NMR (see below).

In a separate experiment styrene was first dimerized completely with CH_3COClO_4 in C_6H_6 at 50 °C[1,2] ($[styrene]_0$ = 0.50 M, $[C]_0$ = 2.0 mM, 2 h) and the crude product was treated in situ with CF_3SO_3H or CH_3COClO_4 (10 mM). The dimerization product, composed of **2** (83 wt %), trimers (14 wt %), and higher oligomers, was readily converted to an oligomeric material (93% yield, 20 min) similar to those obtained from pure dimer **2** in C_6H_6. Addition of a polar solvent, $(CH_2Cl)_2$, prior to treatment with a catalyst increased the total content of trimers and tetramers to 72 wt %.

Oligomerization of pMeSt Dimer. Table III presents the product composition in the oligomerization of pMeSt dimer (1). The data for CH_3COClO_4 were omitted because they were very similar to those for CF_3SO_3H. Figure 3 shows typical MWD curves of the products.

CF_3SO_3H (and CH_3COClO_4) readily converted the pMeSt dimer into oligomeric products that consisted mostly of trimers and tetramers (ca. 90 wt %) in both C_6H_6 and $(CH_2Cl)_2$. The trimer content was always higher than in the corresponding reaction of **2**. $BF_3O(C_2H_5)_2$, inactive toward **2**, also produced oligomers but was less effective than the oxo acid catalysts. The time–conversion profile for the pMeSt dimer (Figure 2) indicates, as expected, that it is more reactive than the styrene dimer.

Depolymerization of Dimer Cations. The formation of styrene trimers from the unsaturated dimer **2** requires the presence of styrene (**4**) and/or its protonated form (the styryl cation, 4^+) in the reaction system. They are most likely produced by the depolymerization of the dimer cation 2^+ (eq 1). Although such depolymerization (fragmentation) processes are well-known in the cationic polymerizations of α-methylstyrene[13,14] and aliphatic olefins,[15,16] the corresponding reaction for styrene has apparently been disregarded. The use of an unsaturated dimer as a starting material has now revealed the presence of this reverse process, which has been undetectable in the conventional polymerization of monomeric styrene. The extremely low equilibrium monomer concentration ($\sim 10^{-6}$ M at 25 °C)[14] and the high heat of polymerization ($-\Delta H$ = 16.7 kcal/mol)[17] for styrene, however, indicate that the propagation is thermodynamically much more favored than the depolymerization. The dimer cation 2^+ may therefore dissociate to the monomeric components (**4** and 4^+) only when it is formed in the absence of the monomer.



Structure of the Products and Oligomerization Pathway. To obtain a more complete mechanistic understanding of the oligomerization of dimers 1 and **2**, we analyzed the structures of the products by ^1H and ^{13}C NMR spectroscopy. Three oligomer samples obtained from styrene dimer (**2**) by CF_3SO_3H (no. 2 and 5, Table II; no. 3, Table I) were separated into dimer to tetramer fractions by preparative GPC. The trimer fractions were very viscous, colorless oils; the tetramer fractions were colorless semisolids.

A dimer fraction obtained at a low conversion (46%) was pure dimer **2** but one at a high conversion (85%) contained both unsaturated (**2**) and cyclic (**2C**) isomers. This shows that the isomerization of **2** into **2C** takes place in the later

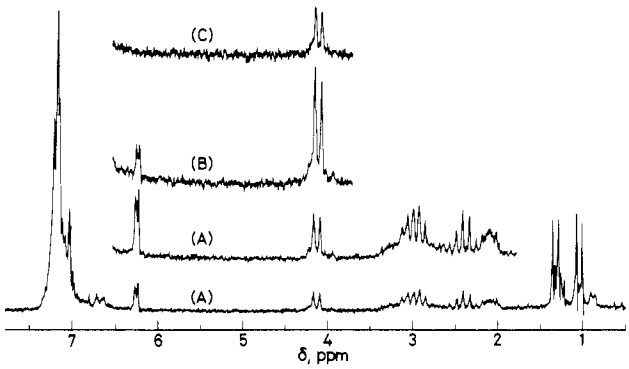


Figure 4. ^{1}H NMR spectra (100 MHz) of the trimer fractions obtained from **2** with CF_3SO_3H in $(CH_2Cl)_2$: $[2]_0$ = 0.10 M. (A, B) $[C]_0$ = 2.0 mM at 50 °C; (C) $[C]_0$ = 10 mM at 70 °C. Dimer conversion: (A) 46%; (B) 85%; (C) 78%.

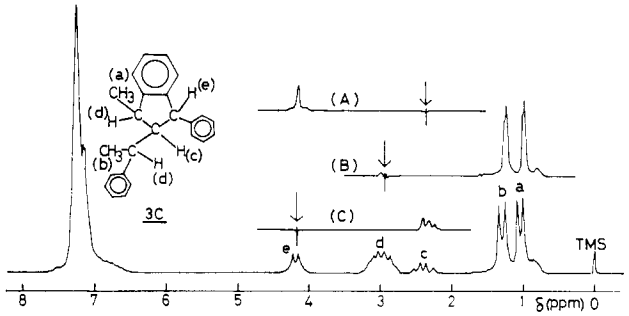
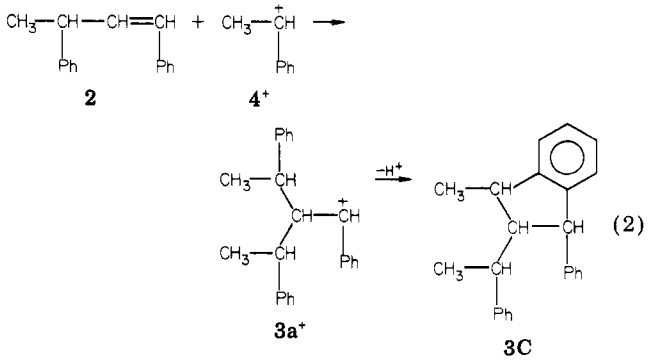


Figure 5. ^{1}H NMR spectra (90 MHz) of the major trimer fraction separated from sample B in Figure 4. (A–C) Decoupled spectra; the arrows indicate the signals of the irradiated proton(s).

stages of the reaction (cf. eq 1). A similar cyclization was also observed for pMeSt dimer (1).

Figure 4 illustrates ^{1}H NMR spectra of the trimer fractions. Inspection of these spectra indicates that the trimer fractions are mixtures of isomers. Spectra A and B, however, exhibit two resonances which are important in deducing the structure of the trimers: a doublet at δ 4.10 associated with Ar_2CH of cyclic end group(s) similar to **2C**[18] and a multiplet at δ 6.23 associated with C=CH of unsaturated terminal(s) as in **2**.

Further separation of the trimer sample B by recycling GPC (recycle, 16 times) gave two well-resolved fractions (2.7:1 by weight). The ^{1}H NMR spectrum of the major fraction (Figure 5) was simple, showing two sharp methyl signals (a and b, δ 1.01 and 1.30) with nearly the same intensity and a doublet (e) at δ 4.17 characteristic of Ar_2CH proton; no olefinic absorptions were detected. On the basis of these spectral features, chemical shifts, and peak multiplicities, this spectrum is assigned to a cyclic trimer **3C** (eq 2). Peak assignments, shown in Figure 5, are



supposed by detailed decoupling experiments. Parts A–C

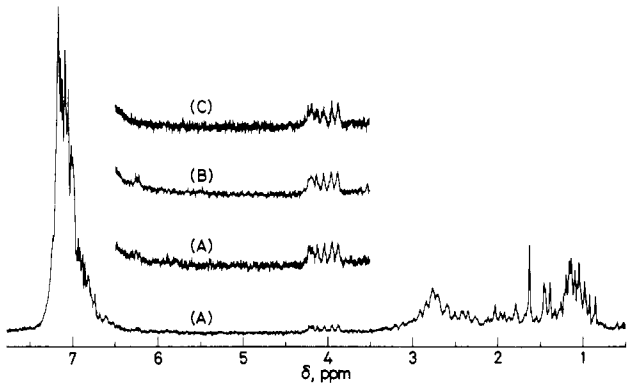


Figure 6. ^{1}H NMR spectra (100 MHz) of the tetramer fractions obtained from **2** with CF_3SO_3H in $(CH_2Cl)_2$. For A–C see Figure 4.

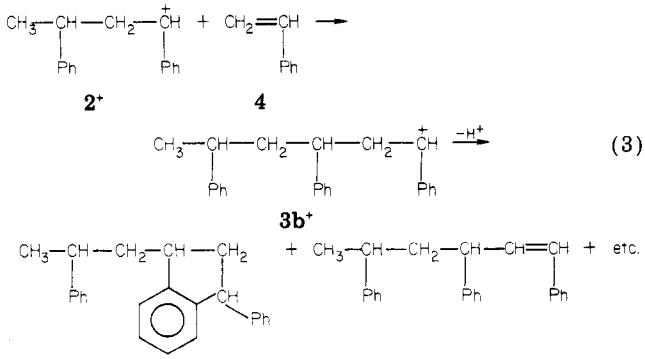
of Figure 5 depict typical examples of the spectral changes on decoupling, which are fully consistent with the proposed structure **3C**.

The ^{13}C NMR spectrum (off-resonance coupled) of the major trimer fraction exhibited six main absorptions of aliphatic carbons: δ 20.7 (q), 21.2 (q), 43.1 (d), 44.7 (d), 55.7 (d), and 63.9 (d). These two methyl and four methine resonances, coupled with the complete absence of methylene units, support strongly the proposed structure **3C**. Equation 2 shows a plausible pathway giving **3C**, where dimer **2** reacts with the styryl cation 4^+ to give intermediate $3a^+$ that subsequently undergoes intramolecular Friedel–Crafts alkylation.

The minor trimer fraction gave complicated ^{1}H and ^{13}C NMR spectra which differed completely from those for the major fraction. This indicates that, after the repeated separation by recycling GPC, the minor fraction is still a mixture of isomers. Its ^{1}H NMR spectrum, however, showed an olefinic peak at δ ~6.3, assignable to unsaturated trimer(s). No further attempt was made to identify this fraction.

Thus, the main trimeric product is the cyclic isomer **3C** formed by the reaction via intermediate $3a^+$ (eq 2). The depolymerization of the dimer cation 2^+ (eq 1) is essential to the formation of trimer **3C**.

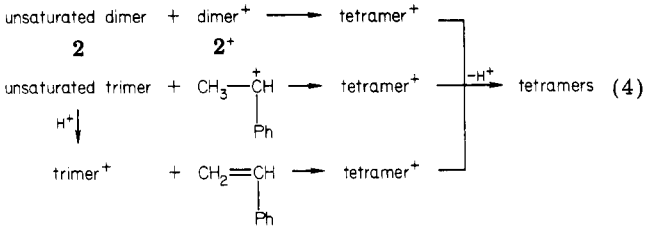
On the other hand, the structural analysis described above also indicates that the total trimer fractions (Figure 4) contain many isomers with cyclic and unsaturated terminals. They may be produced by a number of possible reactions, including the addition of the dimer cation 2^+ to styrene to form a linear trimer cation $3b^+$ (eq 3), hydride transfer in **2**, 2^+, $3a^+$, and $3b^+$, and the like.



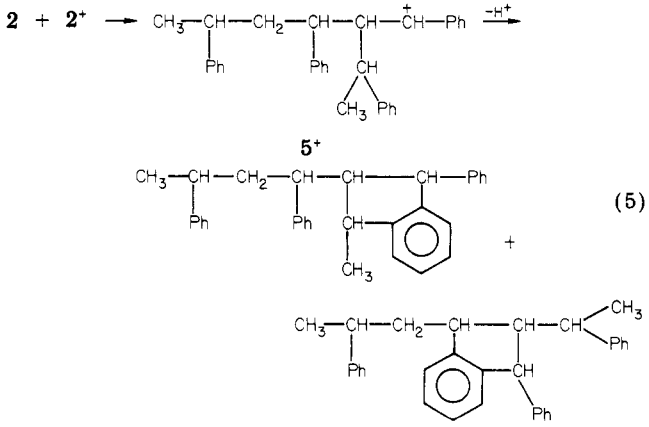
The relative content of the unsaturated trimers clearly decreased with increasing conversion (Figure 4A,B) and none of them were found in a sample obtained at a higher temperature (Figure 4C). These results suggest the conversion of the unsaturated trimers to their cyclic isomers

and/or to higher oligomers in the later stages of the reaction.

Figure 6 depicts ^{1}H NMR spectra of the tetramer fractions produced under the same conditions as for the trimers. No important changes were observed in the ^{1}H NMR spectra with conversion or reaction temperature. The spectra are characterized by the signals in the Ar_2CH region ($\delta \sim 4$) and the virtual absence of olefinic protons (δ 6.2–6.3). These features indicate that the tetramers are predominantly of cyclic end groups (see below). The rather complicated spectra in Figure 6 also indicate the presence of many isomers in the tetramer fractions (an attempt to separate these isomeric tetramers by recycling GPC results in ill-resolved fractions containing two components even after recycling 54 times). The presence of isomeric tetramers seems reasonable in view of the multiple pathways for possible tetramer formation illustrated in eq 4.



Although the difficulty in separation of each tetramer hampered the detailed determination of its structure, the clear Ar_2CH signals around δ 4 (Figure 6) are similar to that for the cyclic trimer **3C** and hence the major part of the tetramers may have cyclic end groups as in **3C**. Equation 5 shows examples of such cyclic tetramers, which



(5)

may be formed from **2** and 2^+ via intramolecular Friedel–Crafts reaction of intermediate 5^+. Similarly, the other pathways given in eq 4 may also yield cyclic tetramers.

A sample obtained from pMeSt dimer (1) (no. 2, Table III; Figure 3b) was also fractionated into dimer to tetramer portions. The dimer fraction consisted mainly of the cyclic isomer. Analysis by ^{1}H NMR spectroscopy showed that the pMeSt trimers and tetramers are similar in structure to the corresponding styrene oligomers, indicating predominant formation of cyclic end groups.

To summarize, the present work has presented evidence for the depolymerization of the propagating dimer cations in the oligomerization of dimers **1** and **2**. The major products were trimers and tetramers with cyclic terminals.

Acknowledgment. We thank Mr. H. Hasegawa of our laboratory for helpful assistance in the NMR measurements.

References and Notes

(1) Sawamoto, M.; Masuda, T.; Nishii, H.; Higashimura, T. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 279.
(2) Higashimura, T.; Nishii, H. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 329.
(3) Higashimura, T.; Hiza, M.; Hasegawa, H. *Macromolecules* **1979**, *12*, 217.
(4) Nishii, H.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1179.
(5) Higashimura, T.; Hiza, M.; Hasegawa, H. *Macromolecules* **1979**, *12*, 1058.
(6) Rosen, M. J. *J. Org. Chem.* **1953**, *18*, 1701.
(7) Corson, B. B.; Dorsky, J.; Nickels, J. E.; Kutz, W. M.; Thayer, H. I. *J. Org. Chem.* **1954**, *19*, 17.
(8) Barton, J. M.; Pepper, D. C. *J. Chem. Soc.* **1964**, 1573.
(9) Bertoli, V.; Plesch, P. H. *J. Chem. Soc. B* **1968**, 1500.
(10) (a) Evans, A. G.; Price, D. *J. Chem. Soc.* **1959**, 2982. (b) Evans, A. G.; Owen, E. D. *Ibid.* **1959**, 4123. (c) Evans, A. G.; James, E. A.; Owen, E. D. *Ibid.* **1961**, 3532.
(11) Masuda, T.; Sawamoto, M.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2981.
(12) Masuda, T.; Higashimura, T. *J. Macromol. Sci., Chem.* **1971**, *5*, 547.
(13) Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1950**, *46*, 331.
(14) Dainton, F. S.; Ivin, K. J. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(15) Schmerling, L.; Ipatieff, V. N. "Advances in Catalysis and Related Subjects"; Frankenburg, W. G., Komarewsky, V. I., Rideal, E. K., Eds.; Academic Press: New York, 1950; Vol. II, pp 34 ff.
(16) Burstall, M. L. "The Chemistry of Cationic Polymerization"; Plesch, P. H., Ed.; Pergamon Press: London, 1963; p 79.
(17) Roberts, D. E.; Walton, W. W.; Jessup, R. S. *J. Polym. Sci.* **1947**, *2*, 420.
(18) Taylor, A. R.; Keen, G. W.; Eisenbraun, E. J. *J. Org. Chem.* **1977**, *42*, 3477.

Free Radical Copolymerization and Cationic Oligomerization of 4,7-Dihydro-1,3-dioxepin. Preparation of Poly[(hydroxymethyl)methylene]

Y. Yokoyama and H. K. Hall, Jr.*

Department of Chemistry, College of Liberal Arts, University of Arizona, Tucson, Arizona 85721. *Received November 21, 1980*

ABSTRACT: Free radical copolymerization of 4,7-dihydro-1,3-dioxepin with maleic anhydride gave 1:1 alternating copolymers possessing modest number-average molecular weights. Reduction with lithium aluminum hydride and hydrolysis of the copolymer gave water-soluble poly[(hydroxymethyl)methylene] with degree of polymerization 10.4–11.2. Cationic homopolymerization of 4,7-dihydro-1,3-dioxepin gave oligomers via ring-opening reaction.

As shown in Schuerch's review on biomedical uses of polysaccharides,[1,2] synthetic water-soluble polymers of well-defined structure will be useful for biomedical applications such as blood volume expanders, neoplastic

0024-9297/81/2214-0471$01.25/0