

C3 Cyclopolymerization VI¹. Direct Observation of the Propagating Species in the Cationic Polymerization of 1,3-Bis(*p*-vinylphenyl)propane in 1,2-Dichloroethane

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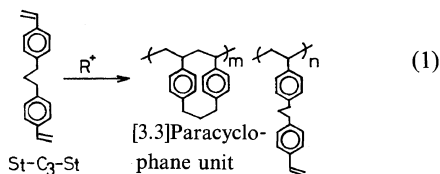
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(Received November 16, 1982)

ABSTRACT: Stopped-flow spectroscopy was used to study the cationic propagating species in the polymerization of 1,3-bis(*p*-vinylphenyl)propane and 1,2-bis(*p*-vinylphenyl)ethane by trifluoromethanesulfonic acid in 1,2-dichloroethane. The cationic species generated from the former monomer was found to show a bathochromically shifted absorption at 360 nm, exceeding those of the cationic species generated from the latter monomer (345 nm) and *p*-methylstyrene (332 nm). This shift is ascribed to the stabilization of the cationic center by an intramolecular through-space interaction with the adjacent terminal styryl group. This stabilization was also suggested by molecular orbital calculation. It is concluded that this interaction facilitates the cyclopolymerization of 1,3-bis(*p*-vinylphenyl)propane.

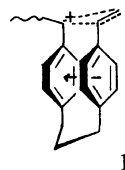
KEY WORDS Cationic Cyclopolymerization / Stopped-Flow Spectroscopy / Styrene Derivatives / Trifluoromethanesulfonic Acid / Cyclic Cation / Molecular Orbital Calculation /

As reported previously,² 1,3-bis(*p*-vinylphenyl)propane (St-C₃-St) is cyclopolymerized only by cationic catalysts to form polymers consisting primarily of [3.3]paracyclophane units (see eq 1). Other initiators such as AIBN, BPO, PhMgBr, *n*-BuLi, Na-Napht., Ni⁰-catalyst, and AlEt₃-TiCl₄ do not give such cyclic units in the main chain.



Therefore, we proposed cation **1** as the intermediate of the cationic cyclopolymerization of St-C₃-St. Cation **1** is stabilized by a through-space interaction with the adjacent terminal styryl group; the two

aromatic rings, illustrated in the formula, are in a face-to-face parallel arrangement.



To demonstrate the existence of this intriguing cationic species, we applied stopped-flow spectroscopy which had been used extensively to observe directly the active species in the cationic polymerization of styrene derivatives.^{3,4} This paper reports the direct observation of cation **1** and discusses its properties in comparison with the propagating species in the cationic polymerization of *p*-methylstyrene.

EXPERIMENTAL

Materials

Monomers, St-C₃-St and 1,2-bis(*p*-vinylphenyl)ethane (St-C₂-St), were prepared and purified as reported previously.^{5,6} Trifluoromethanesulfonic acid (CF₃SO₃H) and stannic chloride (SnCl₄) were purified as reported.⁴ Acetyl perchlorate (AcClO₄) was prepared by a reported method.⁷ 1,2-Dichloroethane (guaranteed reagent) was refluxed over calcium hydride for more than 2 days and distilled just before use.

Procedures

The procedure for stopped-flow spectroscopy using a Union Giken RA-401 spectrophotometer was the same as reported.⁴ Monomer consumption was followed by a rapid quenching of the polymerization mixture with methanol on a Union Giken quenching apparatus. The basic design of our apparatus was according to that of Fresht and Jakes.⁸ It consisted of two four-jet mixers connected in series and two pairs of nitrogen-driven syringes, one for the monomer and initiator solutions and the other for the methanol and solvents. In the first mixer, the monomer and the initiator were mixed to initiate the polymerization and the reaction mixture was introduced, through a Teflon tubing, into the second mixer where it was quenched with methanol. The time lag between initiation and quenching was adjusted electrically by a delay circuit that triggered the two pairs of syringes within a predetermined interval. The shortest time lag was *ca.* 10 ms. The quenched reaction solution was then collected at the outlet of the second mixer for a subsequent determination of the residual monomer by gas chromatography (SE-30 column, oven temperature 220°C, 1,3-bis(*p*-ethylphenyl)propane as an internal standard).

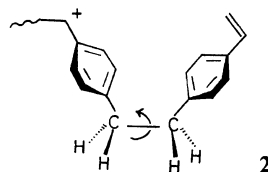
The cyclophane content in a polymer was measured as reported.² Molecular orbital calculation was done at the Data Processing Center of Kyoto Institute of Technology.

RESULTS AND DISCUSSION

Stopped-Flow Spectroscopic Analysis

Figure 1 depicts the stopped-flow absorption spectra of the St-C₂-St/CF₃SO₃H system in 1,2-dichloroethane at 30°C. A transient absorption,

observed at 345 nm, increased rapidly and then gradually decayed. This peak was assigned to the propagating species cation **2** (see below).



In contrast to St-C₃-St, St-C₂-St cannot be cyclopolymerized by any cationic initiators.² This is because the cationic center of **2** cannot reach intramolecularly the terminal double bond; *i.e.*, the face-to-face arrangement of the two adjacent aromatic nuclei, as in **1**, is sterically unfavorable for cation **2**. The absence of such an arrangement is also strongly suggested by fluorescence spectroscopy⁹; 1,2-diphenylethane, similar in structure to St-C₂-St, shows no excimer emission, whereas 1,3-diphenylpropane does.

Cation **2** can be regarded as a model for the linear propagating species **3** of St-C₃-St, since these two intermediates have linear structures and *p*-substituents with almost the same inductive effect.

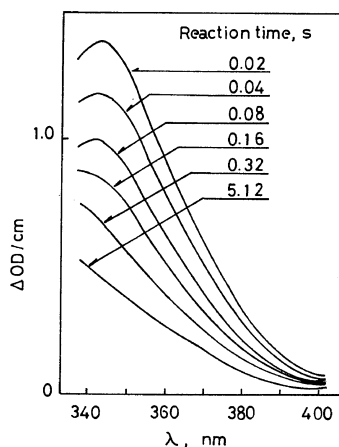
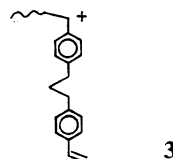


Figure 1. Rapid-scan absorption spectra of the St-C₂-St/CF₃SO₃H system in 1,2-dichloroethane at 30°C: [M]₀ = 20 mM; [C]₀ = 1.0 mM.

In Figure 2, the stopped-flow absorption spectra of the St-C₃-St/CF₃SO₃H system are shown. In this case, an absorption appeared at 360 nm. It rapidly increased and then decreased and was thus assigned to the propagating species for the St-C₃-St polymerization. This assignment is supported by the kinetic data shown below. The absorption shifted to a wavelength 15 nm longer than that of St-C₂-St. This bathochromic shift indicates that in some way, the cationic species generated from St-C₃-St is more stabilized than cation 2. Since the inductive effects of the *p*-substituents in St-C₂-St and St-C₃-St are very similar, the stabilization is not due to a through-bond interaction.

If the observed species was 3, the absorption would appear at about 345 nm as in the case of 2, rather than at 360 nm. Moreover, poly(St-C₃-St), obtained under conditions similar to those for the spectroscopic measurements, contained 84% [3.3]-paracyclophane units in the main chain. Taking

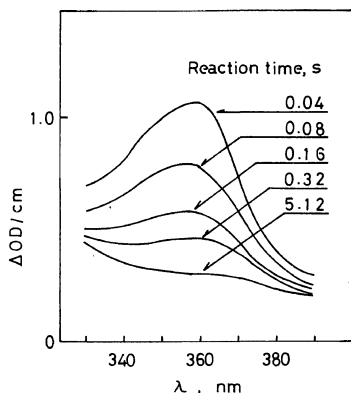


Figure 2. Rapid-scan absorption spectra of the St-C₃-St/CF₃SO₃H system in 1,2-dichloroethane at 30°C: [M]₀ = 20 mM; [C]₀ = 1.0 mM.

these findings into consideration, we conclude that the absorption is ascribed to the intramolecularly stabilized cation 1.

Other initiators such as AcClO₄ and SnCl₄ gave absorptions at the same wavelength (360 nm). Therefore, the species having an absorption at 360 nm is not specific for the CF₃SO₃H-initiated system.

Kinetics

The change in absorption at 360 nm with time in the St-C₃-St/CF₃SO₃H system is shown in Figure 3. It became maximum in 50 ms and then decreased gradually. The concentration of the propagating species was calculated on the assumption that its molar extinction coefficient at 360 nm is the same as that of the living polystyryl anion ($1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).^{4,10,11}

Along with the spectroscopic measurements, the polymerization of St-C₃-St with CF₃SO₃H was carried out under the same conditions, and the

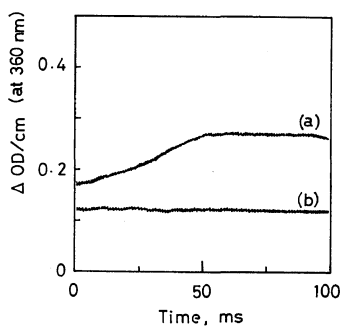


Figure 3. Absorbance change at 360 nm (trace a) in the polymerization of St-C₃-St by CF₃SO₃H in 1,2-dichloroethane at 30°C: [M]₀ = 20 mM; [C]₀ = 0.25 mM. Trace b indicates the absorbance of only the monomer solution recorded under the same detector conditions.

Table I. Cationic polymerizations of styrene derivatives by CF₃SO₃H in 1,2-dichloroethane at 30°C

Monomer	[M] ₀ × 10 ³	[C] ₀ × 10 ³	λ _{max}	k _p × 10 ⁻³	[P*] _{max} /[C] ₀
	mM	mM			
<i>p</i> -MeSt ^a	20	1.0	332	120	1.4
St ^a	20	5.0	340	130	0.5
St ^b	397	5.3	340	200	1.2
St-C ₃ -St	20	0.25	360	36	7.0
St-C ₂ -St	20	1.0	345	—	—

^a Reference 10. ^b Reference 11.

monomer conversion was determined by rapid-quenching (Figure 4). The decrease in monomer concentration could not be followed spectroscopically, since its initial value was too high (20 mM). From the data shown in Figures 3 and 4, the k_p value was obtained on the basis of the following equation³:

$$\ln \left[\frac{[M]_{t_1}}{[M]_{t_2}} \right] = \frac{k_p}{\epsilon_{360}} \int_{t_1}^{t_2} \Delta OD_{360} dt \quad (2)$$

where ΔOD_{360} is the absorbance at 360 nm. The value, $\ln([M]_{t_1}/[M]_{t_2})$, was obtained from the smoothed time vs. conversion plot shown in Figure 4. Plotting it against $\int \Delta OD dt$ gave a straight line passing through the origin (Figure 5). Therefore, the absorption observed at 360 nm should be assigned to the propagating species for the St-C₃-St polymerization.

The values of k_p and the maximum concentration

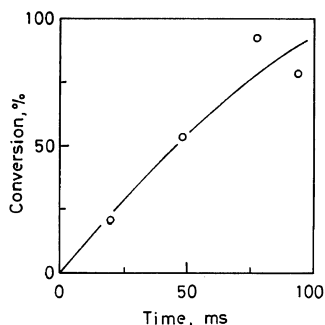


Figure 4. Time-course of the polymerization of St-C₃-St in 1,2-dichloroethane at 30°C: $[M]_0 = 20$ mM; $[C]_0 = 0.25$ mM.

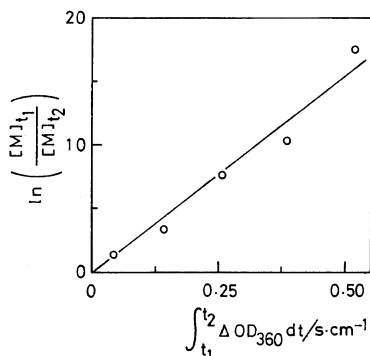
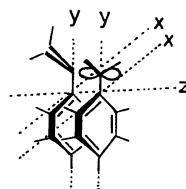


Figure 5. Plot of eq 2 for the polymerization of St-C₃-St in 1,2-dichloroethane at 30°C: $[M]_0 = 20$ mM; $[C]_0 = 0.25$ mM.

of the propagating species are summarized in Table I together with those of styrene^{10,11} and *p*-methylstyrene.⁴ When compared with *p*-methylstyrene, St-C₃-St gave a smaller k_p and a higher $[P^*]_{\max}/[C]_0$. This suggests strongly that species **1** is more stabilized than the propagating species of *p*-methylstyrene.

Molecular Orbital Calculation

To understand how cation **1** is stabilized, perturbation treatment was applied to a benzyl cation and styrene pair in a through-space interaction as a model for **1**. Molecular orbitals were calculated by the CNDO/2 method. The arrangement of the two molecules for the calculation is shown below.



The two benzene nuclei were arranged in parallel, 3.14 Å apart, which is the distance between the two aromatic rings of [3.3]paracyclophane determined by X-ray crystallography.¹²

The total delocalization energy for the benzyl cation-styrene pair was calculated to be 10.7 kcal mol⁻¹ (0.4625 eV). The value is much greater than the trimethylene gauche-repulsive energy (3.6 kcal mol⁻¹),¹³ which is involved in the formation of cation **1**. This means that cation **3** easily cyclizes itself to become a much stabilized cation **1**. Therefore, the calculation supports the existence of an intramolecularly stabilized cation like **1**. Similar through-space stabilization has been proposed for carbocations similar to **1**.¹⁴⁻¹⁶

Moreover, one third of the strain energy of [3.3]paracyclophane (12 kcal mol⁻¹)¹⁷ is considered due to aromatic ring repulsion¹⁸ which is almost entirely absent in cation **1**; thus the calculated stabilization energy of cation **1** is sufficient to lower the transition state potential to form the [3.3]paracyclophane unit.

In this paper, we are proposing a nonclassical structure with a two-electron-three-center bond for cation **1**. Although the classical [3.3]paracyclophanyl cation is also conceivable as the propagating species for the cyclopolymerization of St-C₃-St, its vacant *p*-orbital cannot conjugate fully with the

π -orbital of the adjacent benzene ring, because of high strain. Consequently, the cation cannot be stabilized to the same extent as even its non-cyclic counterpart **3**. This is contrary to our spectroscopic observation indicating some stabilization of the propagating species. Hence, the classical cation is not likely in our system.

In conclusion, the existence of the intramolecularly stabilized cation **1** was demonstrated by stopped-flow absorption spectroscopy and the stabilization of this cation is concluded to facilitate the cyclopolymerization of St-C₃-St.

Acknowledgement. We thank Dr. Takuji Sugimoto, School of Medicine, Osaka University, for kindly providing the computation program.

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