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Photoinduced Radical Polymerization of Styrene Derivatives via Their Cation Radicals

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Summary

It was found that radical polymerization occurs when the mixture of p-methoxystyrene and styrene in the presence of electron acceptors is photoexcited in basic solvents. Concomitantly, p-methoxystyrene-styrene co-dimers: trans-1-(4'-methoxyphenyl)-2-phenylcyclobutane and 1-(4'-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene are produced. From the results of some polymerization runs and the co-dimer structure, it is considered that the linear co-dimer cation radical is the common precursor for both radical polymerization and cationic dimerization, and the radical polymerization is initiated by its radical end.

Introduction

Cation radicals of vinyl monomers are rather newly established intermediates (LEDWITH, 1976). It is interesting that the cation radicals may react in both cationic and radical nature. But the reactivity of cation radicals is still not well understood.

Our recent investigations indicate that photochemically produced cation radicals of styrene derivatives undergo cationic dimerization (YAMAMOTO et al., 1975, ASANUMA et al., 1975a and b) and cationic polymerization (in halogenated solvents, GOTOH et al., 1979). These reaction manners are understood as the predominant reactivities of the cation ends of the intermediary dimer cation radicals.

However, there is no report on the reactivity of radical ends. Only radical polymerization of styrene was reported in the presence of pyromellitic dianhydride (SUZUKI et al., 1976). But in this case, the initiating precursor is thought to be the excited charge-transfer complex itself before ionic dissociation.

We now report the radical polymerization presumably initiated by the radical end of the co-dimer cation radical.

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Experimental

Monomers, p-methoxystyrene(p-MeOSt) and styrene (St), and solvents, acetonitrile(ACN) and tetrahydrofuran(THF), were purified and dried by the usual procedures. Acceptors, m-dicyanobenzene(m-DCNB) and dimethyl terephthalate(DMTP), were purified by repeated recrystallization. Sample solutions were pipetted into Pyrex polymerization ampoules and they were completely degassed by freeze-pump-thaw cycles ($<2 \times 10^{-6}$ Torr). Photoirradiation was carried out with 300 W high-pressure Hg lamp (Toshiba 300H) for 3 hr at appropriate temperatures in water bath.

After irradiation, ampoules were quickly opened, and the solvents were evaporated. Residues were dissolved in THF, and they were measured with a gel permeation chromatograph (GPC)(Toyo Soda HLC 802-UR). Conversion and molecular weight of polymers were calculated from GPC charts. Dimer fractions were further analyzed by a gas-liquid phase chromatograph (GLPC) (Shimadzu GC-6A), with raising the temperature from 235 to 270°C, using a column packed Apiezon Grease L (2m). Polymers were precipitated off with hexane before injection. In these works, o-nitrobiphenyl was used as an internal standard. Dimers were isolated with GLPC. ^{1}H-NMR and MS spectra were obtained with a Varian HA-100 using Me_4Si as an internal standard and a Hitachi M-52 gas chromatograph-mass spectrometer, respectively.

Results and Discussion

FIGURE 1 shows the absorption spectra of the reaction systems. The wavelength of the main exciting light through Pyrex glass is 313 nm, hence, the main excited species is p-MeOSt. Acceptors used in this experiment are appropriate for p-MeOSt to produce its cation radical through exciplex mechanism (YAMAMOTO et al., 1975).

TABLE I summerizes the results of polymerization. The polymerization was initiated photochemically in the presence of acceptor, only when both monomers exist in the system. ACN could be replaced by THF, and DMTP is also effective similarly to m-DCNB. These results suggest that the polymerization is initiated by the p-MeOSt-St co-dimer cation radical ((III) in the SCHEME).

The Arrhenius plots of the molecular weight of the polymer($\bar{M}_n$) and the polymerization rate(R_p) are shown in FIGURE 2. The overall activation energies are 4.8 kcal/mol for $\bar{M}_n$ and 5.9 kcal/mol for R_p. For photoinduced cationic polymerization of St, the activation energies of $\bar{M}_n$ and R_p are negative (SUZUKI et al., 1976, GOTOH et al., 1979). In the present system, GPC analysis shows unimodal molecular weight distribution of the polymers. Since solvents are basic, cationic polymerization can hardly proceed. These results indicate that the initiation should occur only from radical end of the co-dimer cation radical (III).

A typical chart of GLPC for the dimer fraction is shown in FIGURE 3. Co-dimers 6 and 7 were assigned to be *trans*-1-(4'-methoxyphenyl)-2-phenylcyclobutane and 1-(4'-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene, respectively.

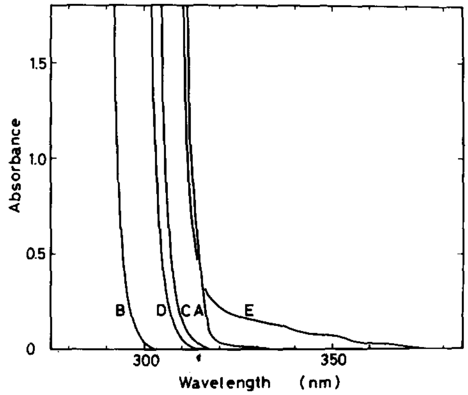

FIGURE 1 Absorption spectra of *p*-MeOSt(A)(38.0 mM), *m*-DCNB(B)(22.4 mM), DMTP(C)(22.4 mM), and St(D and E) (1.0 and 8.6 M, respectively) at room temperature in ACN.

TABLE I Photopolymerization of *p*-MeOSt-St-Acceptor systems.

Exp. No.	St (M)	*p*-MeOSt (mM)	Acceptor (22.4 mM)	Solvent	Temp. (°C)	Time (h)	Polymer* Yield(%)
1	1.0	-	*m*-DCNB	ACN	45	3	0
2	-	660	*m*-DCNB	ACN	45	3	0
3	1.0	38	-	ACN	50	3	0
4	1.0	38	*m*-DCNB	ACN	50	12**	0
5	1.0	38	*m*-DCNB	ACN	50	3	6.2
6	1.0	38	DMTP	ACN	50	3	4.0
7	1.0	38	*m*-DCNB	THF	45	3	4.3
8	1.0	38	DMTP	THF	45	3	3.4
9	8.6	38	*m*-DCNB	-	40	3	2.2***

* Based on St. ** In the dark. *** $\overline{M}_n$ is 59000.

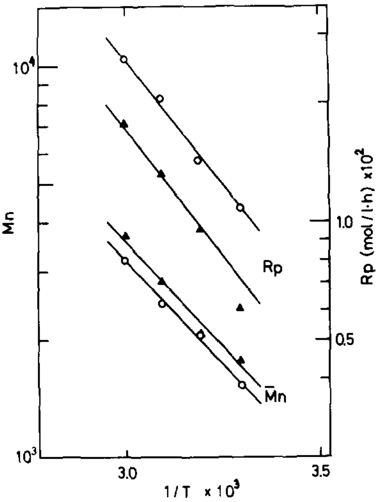

FIGURE 2 Arrhenius plots of $\bar{M}_n$ and R_p. St(1.0 M), *p*-MeOSt(38.0 mM), o: *m*-DCNB(22.4 mM), ▲: DMTP (22.4 mM) in ACN solvent.

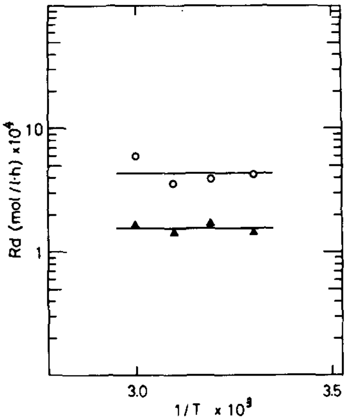

FIGURE 4 Arrhenius plot of R_d. Reaction condition is the same as in FIGURE 2.

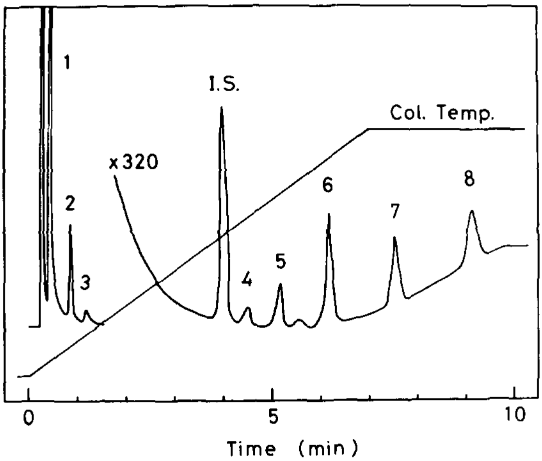

FIGURE 3 GLPC chart of the dimer fraction for *p*-MeOSt -St-Acceptor system: St(1), *p*-MeOSt(2), *m*-DCNB(3), St homo-dimers(4 and 5, *cis*- and *trans*-1,2-diphenylcyclobutane, respectively), *p*-MeOSt-St co-dimers(6 and 7), and *p*-MeOSt homo-dimer(8, 7-methoxy-(4'-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene [Usually, *p*-MeOSt homo-dimer is of cyclobutane type, but in the presence of a large amount of aromatic compounds, tetrahydronaphthalene type one is specifically produced.]).

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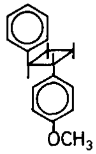

^{1}H-NMR: (CCl_4), δ 1.86-2.46(m,4H,CH_2), 3.35-3.58(m,2H,CH), 3.72(s,3H,OCH_3), 6.66-7.34(m,9H,aromatic).

MS: m/e 238(M^+), 210(M^+-ethylene), 134, 119, 104.

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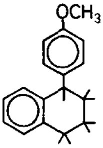
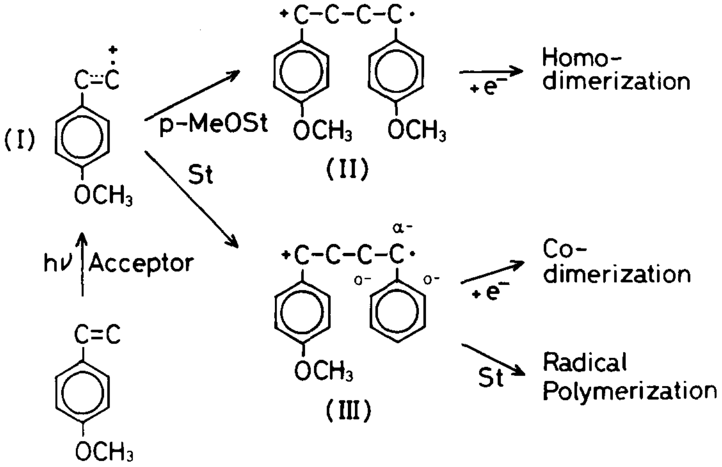


^{1}H-NMR: ($CDCl_3$), δ 1.76-2.34(m,4H,CH_2), 2.74-2.96(m,2H,CH_2), 3.78(s,3H,OCH_3), 3.95-4.14(m,1H,CH), 6.70-7.24(m,8H,aromatic).

MS: m/e 238(M^+), 210(M^+-ethylene), 134, 129.

The tetrahydronaphthalene type dimer of St could not be detected, so the cation radical transfer (ASANUMA et al., 1977) from p-MeOSt monomer cation radical (I) to St can be omitted. The structure of co-dimer 7 indicates that the cation is on the α-carbon of p-MeOSt unit of the co-dimer cation radical (III) as shown in SCHEME.



SCHEME

The homo-dimerization of p-MeOSt is much more dominant compared with the co-dimerization (the estimated reactivity ratio is ca. 100), although the reactivities of these monomers to the p-MeOSt radical are almost the same. The overall activation energy of the co-dimerization rate (R_d) is almost zero as shown in FIGURE 4. These results show that the co-dimerization reaction proceeds in cationic nature.

In less basic solvents, cationic dimerization and polymerization, but not radical polymerization were observed for the homo-dimer cation radical (II)(GOTOH et al., to be published). This fact indicates much higher reactivity of the cation end than that of the radical end of this intermediate. It was also observed that the cationic dimerization is predominant compared with the initiation of cationic polymerization. This result means that the rate of intramolecular cyclization is much larger than that of intermolecular addition reaction (initiation reaction) under the monomer concentration used in the study (1.5 mol/l). Similar behaviors were also observed for the homo-dimer cation radical of styrene in methylene chloride solvent (GOTOH et al., 1979).

In basic solvents, only cationic dimerization was observed for the homo-dimer cation radical (II) (YAMAMOTO et al., 1975, and this work), while cationic dimerization and radical polymerization occurred for the co-dimer cation radical (III). In this system, the concentration of the initiating species for the radical polymerization was estimated to be in the same order of that for the co-dimerization. The lack of radical polymerization for the homo-dimer cation radical (II) seems to be not by the deppression of radical reactivity, but due to the enhancement of the cationic dimerization rate which is caused by the higher electron density on the α-carbon induced by p-methoxy substituent, although the reactivity of the cation end is considerably suppressed by solvation. Radical polymerization observed for the co-dimer cation radical (III) in basic solvents seems to appear by the suppression of cationic dimerization rate, which is caused firstly by the stabilization of the cation end by solvation, and secondly by the lower electron densities on α- and o-carbon of styrene unit.

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