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Anionic Copolymerization of Styrene and *trans*-Stilbene with *n*-Butyllithium

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The anionic copolymerization of styrene (M_1) and *trans*-stilbene (M_2) by *n*-butyllithium was investigated. *trans*-stilbene, which can not homopolymerized by itself, could be copolymerized with styrene in tetrahydrofuran and in benzene by an anionic catalyst. The copolymerization in tetrahydrofuran proceeded with a chain transfer to *trans*-stilbene, while that in benzene seemed to proceed without the chain transfer. The monomer reactivity ratio, r_1, was obtained from the copolymer composition at the complete consumption of M_1, assuming that the rate constant, k_{22}, is zero. The r_1 values were 2.3 in tetrahydrofuran at 0°C and 18 in benzene at 30°C. The color of the solution changed from red to purple in tetrahydrofuran, while in benzene no change occurred.

The present authors have found that, if a suitable combination of monomers is chosen, an alternating copolymer can be obtained by an anionic mechanism.[1] In the previous paper, an investigation of the anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2) was reported in detail.[2] The copolymerization proceeded in a living system, and monomer reactivity ratios, r_1, were obtained as 0.2 in tetrahydrofuran (THF) at 30°C and as 0.4 in benzene at 30°C, assuming that a 1,1-diphenylethylene anion does not add to 1,1-diphenylethylene.

In this paper, a detailed study of the copolymerization of styrene (M_1) and *trans*-stilbene (M_2) will be described, and the results will be correlated with the results of the copolymerization of styrene and 1,1-diphenylethylene.

Experimental

Materials. *Styrene*. This was purified by the usual method and was distilled on a vacuum line from calcium hydride.

trans-Stilbene. The monomer synthesized from benzoin[3] was recrystallized from methanol and then twice from *n*-hexane.

Tetrahydrofuran (*THF*). The solvent, refluxed over metallic sodium and then over lithium aluminum hydride, was distilled onto sodium-potassium alloy and naphthalene. From the characteristic green solution, it was then distilled on a vacuum line to a reaction vessel.

Benzene. Benzene was purified by the standard method[4] and was stored over sodium. Before use, it was transferred to a flask containing *n*-butyllithium, and then it was distilled on a vacuum system to a reaction vessel.

n-Butyllithium (*n-BuLi*). According to the method of Ziegler,[5] *n*-BuLi was prepared in *n*-heptane and the concentration was determined by double titration.[6]

Polymerization. *trans*-Stilbene was first placed in a glass ampoule and dried *in vacuo*. Then, the solvent and styrene were transferred into the ampoule by vacuum distillation. The solution was immersed in a bath at a constant temperature, and *n*-BuLi was added under dry argon with a syringe. The reaction was terminated by adding methanol, after which the contents of the ampoule were poured into a large amount of methanol. The precipitated polymer was collected by filtration, washed with methanol, dried, and weighed. The mother liquor and the washings of the polymer precipitation were then combined and evaporated at reduced pressure, and the residual unchanged monomer and lithium compound were weighed.

Measurement. *Viscosity*. The viscosity of the polymer was measured in a benzene solution (C= 1.0 g/d*l*) at 30.0°C.

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2) H. Yuki, J. Hotta, Y. Okamoto and S. Murahashi, This Bulletin, **40**, 2659 (1967).

3) R. L. Shriner and A. Berger, "Organic Syntheses," Coll. Vol. III, p. 786 (1955).

4) A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd. Ed., Interscience Publishers, New York (1955).

5) K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

6) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

Electronic Spectrum. The spectrum of a living anion was measured in THF with a Cary 15 Spectrophotometer.

Results

Polymerization in THF. The copolymerization of styrene (M_1) and *trans*-stilbene (M_2) with *n*-BuLi was carried out in THF at 0°C, the initial molar ratio of styrene to *trans*-stilbene, $[M_1]_0/[M_2]_0$, being 1.0/1.5. The results are shown in Fig. 1. The reaction came instantaneously to an end, always giving a copolymer in a 68% yield against the total amount of monomers, regardless of the reaction time measured.

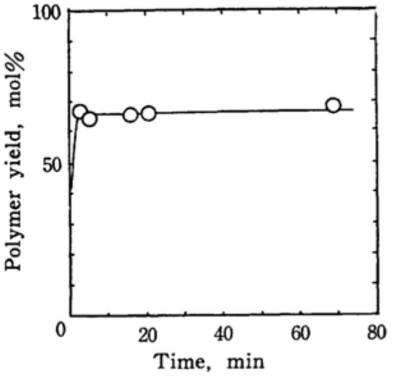


Fig. 1. Anionic copolymerization of styrene (M_1) and *trans*-stilbene (M_2) in THF.—Time *vs.* polymer yield.

$[M_1]_0+[M_2]_0$ 7.0 mmol, $[M_1]_0/[M_2]_0$ 1/1.5, THF 15 m*l*, Temp. 0°C, *n*-BuLi 5.8×10^{-2} mmol.

The copolymerization was carried out by varying the ratio, $[M_1]_0/[M_2]_0$, the total amounts of monomers, $[M_1]_0+[M_2]_0$, being kept constant. The results are summarized in Table 1. Attempts to determine the copolymer composition were made with elementary analysis, UV and NMR spectroscopies, but no satisfactory results were obtained because these monomers all have similar structures. On the other hand, the residues recovered from the mother liquor of polymer precipitates were solid and were found to be a mixture of lithium compounds, mainly carbonate, and unchanged *trans*-stilbene, which was identified by IR and UV spectroscopies. The sum of the amounts of the polymer and the unchanged monomer, $P+M_r$, just balanced the total amounts (weight) of the monomers, M_1+M_2, indicating the complete incorporation of the charged styrene into the copolymer. The amount of unchanged *trans*-stilbene was also determined by studying the UV spectrum of a part of the reaction mixture; it was found to be nearly equal to the value obtained by gravimetry. Thus, the copolymer composition can be determined from the polymer yield as $M_1/P-M_1$; this value is converted into the molar ratio of the monomers in the copolymer, $[m_1]/[m_2]$, in Table 1. Below, the composition of the copolymer is always calculated from the polymer yield on the assumption that the charged styrene is completely consumed by the copolymerization. We have found that the polymer yield and the $[m_1]/[m_2]$ ratio decrease with a decrease in the $[M_1]_0/[M_2]_0$ ratio.

The copolymerization at 0°C in THF was investigated by varying the ratio, $[M_1]_0/[M_2]_0$, while the amount of the M_1 monomer was kept constant. The results are listed in Table

TABLE 1. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND *trans*-STILBENE (M_2) IN THF

$[M_1]_0+[M_2]_0$ 3.4 mmol, [*n*-BuLi] 5.7×10^{-2} mmol, THF 10 m*l*, temp. 0°C, time 40—60 min

Monomer, g		$[M_1]_0/[M_2]_0$ [a]	Polymer	Unchanged M_2		$[m_1]/[m_2]$ [d]
M_1	M_2		P, g	M_r, g [b]	M_r, g [c]	
0.244	0.187	2.26	0.353	0.080	0.059	3.9
0.206	0.250	1.42	0.338	0.127	0.100	2.7
0.170	0.314	0.94	0.320	0.165	0.118	2.0
0.140	0.374	0.65	0.285	0.235	0.191	1.7

a) Initial molar ratio in monomer mixture.
b) Obtained by gravimetry. Weight (8 mg) of Li_2CO_3 was subtracted from the weight of residue obtained from mother liquor of polymer.
c) Estimated from UV spectrum.
d) Molar ratio of monomers in copolymer.

TABLE 2. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND *trans*-STILBENE (M_2) IN THF

$[M_1]_0$ 3.47 mmol, THF 15 m*l*,
[*n*-BuLi] 5.7×10^{-2} mmol, temp. 0°C, time 2.5 hr

$[M_2]_0$ mmol	$[M_1]_0/[M_2]_0$ [a]	Yield %	$[m_1]/[m_2]$ [b]	η_{sp}/c [c] d*l*/g	s. p. [d] °C
0.41	8.09	85.5	43	0.652	135
0.92	3.76	85.6	6.8	0.391	157
1.26	2.71	87.0	4.2	0.296	160
2.34	1.50	79.6	2.4	0.188	165
3.44	1.00	72.8	1.8	0.126	176
5.28	0.67	62.5	1.4	0.104	190
8.12	0.43	51.1	1.1	0.010	200

a) Initial molar ratio in monomer mixture.
b) Molar ratio of monomers in copolymer.
c) Benzene solution at 30.0°C.
d) Softening point of copolymer.

2. The polymer yield against the total amount of the monomers, the copolymer composition expressed in the $[m_1]/[m_2]$ ratio, and the viscosity of the polymer all decreased with an increase in the amount of M_2 in the monomers charged, while the softening point rose. The data in Table 2 suggest that a lower monomer composition, $[M_1]_0/[M_2]_0$, than 0.4 may give an essentially alternating copolymer of M_1 and M_2 monomers with a very low molecular weight.

If, in the copolymerization, the M_2 monomer can not add to the $\sim\!\sim M_2^-$ anion, and if the M_1 comonomer is completely incorporated into the copolymer, the monomer reactivity ratio, r_1, can easily be obtained from the polymer yield by assuming that $k_{22}=0$ and $[M_1]=0$ in the Mayo-Lewis copolymer composition equation.[2] The copolymerization in THF at 0°C gave the value, $r_1=2.3$, as is show in Fig. 2, the plots in which were obtained from the data in Tables 1 and 2.

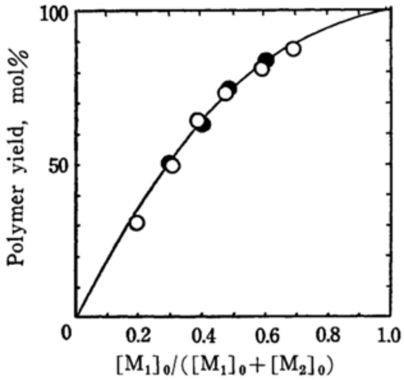


Fig. 2. Anionic copolymerization of styrene (M_1) and *trans*-stilbene (M_2) in THF.—Monomer reactivity ratio, r_1.

○: $[M_1]_0+[M_2]_0$ 3.4 mmol, THF 10 m*l*, Time 40—60 min

●: $[M_1]_0$ 3.47 mmol, THF 15 m*l*, Time 2.5 hr, *n*-BuLi 5.7×10^{-2} mmol, Temp. 0°C

Polymerization in Benzene. The reaction rate was investigated in the copolymerization in benzene with *n*-BuLi at 30°C; the molar ratio of the initial monomer concentrations, $[M_1]_0/[M_2]_0$, was 1.0/3.0. The results are shown in Fig. 3. The reaction proceeded slowly in comparison with that in THF, a constant yield (24%) being obtained after about 24 hr. It was confirmed that, in this case, styrene was also completely incorporated into the copolymer after a sufficient reaction time.

The effects of the initial molar ratio, $[M_1]_0/[M_2]_0$, on the copolymerizaton in

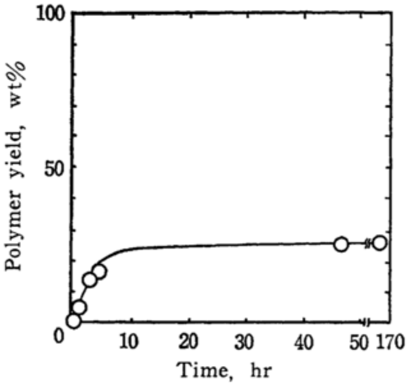


Fig. 3. Anionic copolymerization of styrene (M_1) and *trans*-stilbene (M_2) in benzene.—Time *vs.* polymer yield.

$[M_1]_0+[M_2]_0$ 14.8 mmol, $[M_1]_0/[M_2]_0$ 1.0/3.0, Benzene 20 m*l*, Temp. 30°C, *n*-BuLi 1.14×10^{-1} mmol.

TABLE 3. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND *trans*-STILBENE (M_2) IN BENZENE

$[M_1]_0$ 3.4 mmol, benzene 15 m*l*, [*n*-BuLi] 1.14×10^{-1} mmol, temp. 30°C, time 90 hr

$[M_2]$ mmol	$\frac{[M_1]_0}{[M_2]_0}$ a)	Yield %	$\frac{[m_1]}{[m_2]}$ b)	η_{sp}/c c) dl/g
0.38	9.00	85.1	99	0.095
0.87	4.00	75.1	19	0.099
1.49	1.90	63.7	13	0.105
2.33	1.44	54.5	9.0	0.093
3.51	0.96	45.2	6.7	0.145
5.26	0.64	36.9	4.9	0.132
7.13	0.47	31.4	3.8	0.101

a) Initial molar ratio in monomer mixture.
b) Molar ratio of monomers in copolymer.
c) Benzene solution at 30.0°C.

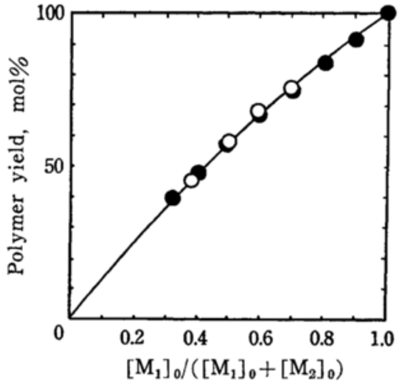


Fig. 4. Anionic copolymerization of styrene (M_1) and *trans*-stilbene (M_2) in benzene.—Monomer reactivity ratio, r_1.

○: $[M_1]_0+[M_2]_0$ 8.0 mmol, ●: $[M_1]_0$ 3.4 mmol, Benzene 15 m*l*, Cat. *n*-BuLi, Temp. 30°C, Time: ○ 40 hr, ● 90 hr.

benzene were investigated with a constant concentration of the M_1 monomer. The results are listed in Table 3. The relative reactivity of styrene against *trans*-stilbene was much greater in benzene than in THF. The solution viscosity of the polymer was constant regardless of $[M_1]_0/[M_2]_0$.

The monomer reactivity ratio, r_1, was calculated from the polymer yield as has been described above. As Fig. 4 shows, r_1 is 18 in the copolymerization in benzene at 30°C.

Electronic Spectrum of the Reaction Mixture. In the copolymerization of styrene and *trans*-stilbene by *n*-BuLi in THF, the red color gradually turned purple, even at 0°C. The change in the electronic spectra of the solution was followed; it is shown in Fig. 5. The red color of the solution diminished gradually and an absorption appeared at 555 mμ after about 30 min, by which time the copolymerization reaction had already finished. In the homopolymerization of styrene carried out under the same conditions, the red color of the reaction mixture did not change when it stood for a prolonged period. Therefore, this change in spectra may be attributed to the anion of *trans*-stilbene. The same spectral change was also observed in the reaction of *trans*-stilbene with *n*-BuLi in THF.[7] The purple solution initiated the polymerization of styrene to give a polymer quantitatively. On the other hand, in the copolymerization in benzene the orange color of the solution did not change in several hours, even at 30°C.

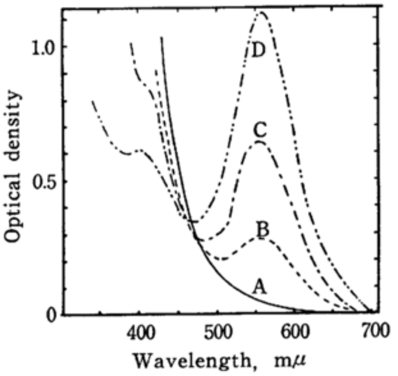
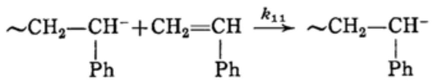


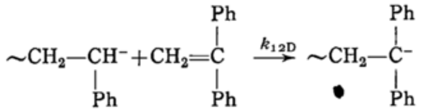
Fig. 5. Anionic copolymerization of styrene (M_1) and *trans*-stilbene (M_2) in THF.—Electronic spectra of reaction mixture.

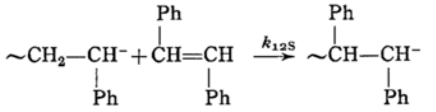
$[M_1]_0+[M_2]_0$ 8.8 mmol, Cat. *n*-BuLi, Temp. 0°C, Time: A 20 min, B 33 min, C 1.6 hr, D 4.8 hr

Discussion

Reactivity of Monomers. The monomer reactivity ratios, r, in the copolymerization of styrene (M_1) and *trans*-stilbene (M_2) or 1,1-diphenylethylene (M_2)[2] with *n*-BuLi are summarized in Table 4. The r_1 values obtained in the copolymerization with 1,1-diphenylethylene were less than unity in THF and also in benzene, while the ratios in the copolymerization with *trans*-stilbene were more than unity in both the solvents. These results show that, in the following reactions, the order of the rate constants is $k_{12D}>k_{11}>k_{12S}$.


$$\sim CH_2-\underset{Ph}{CH^-}+CH_2=\underset{Ph}{CH} \xrightarrow{k_{11}} \sim CH_2-\underset{Ph}{CH^-} \qquad (1)$$


$$\sim CH_2-\underset{Ph}{CH^-}+CH_2=\overset{Ph}{\underset{Ph}{C}} \xrightarrow{k_{12D}} \sim CH_2-\overset{Ph}{\underset{Ph}{C^-}} \qquad (2)$$


$$\sim CH_2-\underset{Ph}{CH^-}+\overset{Ph}{CH}=\underset{Ph}{CH} \xrightarrow{k_{12S}} \sim \overset{Ph}{CH}-\underset{Ph}{CH^-} \qquad (3)$$

1,1-Diphenylethylene is the most reactive monomer to a styryl anion, for the monomer reacts with the anion to give a more stable anion conjugating with two benzene rings. On the other hand, *trans*-stilbene is the least reactive monomer because of its steric hindrance. The copolymerization of styrene and *trans*-stilbene in THF proceeded rapidly, while the copolymerization of styrene and 1,1-diphenylethylene proceeded so slowly that the reaction finished in 24 hr, even in THF at 0°C.[2] This may have been because the *trans*-stilbene anion produced in the reaction (3) has the same structure as the styryl anion, which is reactive enough to end instantaneously the homopolymerization of styrene, while the 1,1-diphenylethylene anion is very stable and has a big steric hindrance, therefore giving a very small k_{21}.

As Figs. 1 and 3 show, the overall rate of the copolymerization is greater in THF than in benzene. This may be becanse in THF a free ion plays a great part in the chain growth,[8] while in benzene living chain ends form ion pairs to associate themselves.[9] The

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[8] D.N. Bhattachayryya, C.L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); H. Hostalka, R.V. Figini and G.V. Schulz, *Makromol. Chem.*, **71**, 198 (1964).

[9] D.J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960); M. Morton, L.J. Fetters and E. E. Bostick, *J. Polymer Sci.*, **C1**, 311 (1963).

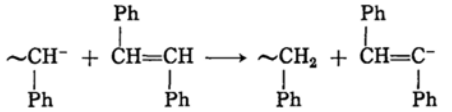
TABLE 4. MONOMER REACTIVITY RATIO, r_1, IN ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND 1, 1-DIPHENYLETHYLENE (M_2)2) OR *trans*-STILBENE (M_2) WITH *n*-BULI

Monomer		r_1 value	
M_1	M_2	in THF	in Benzeen
Styrene	1, 1-Diphenyl-ethylene	0.13a)	0.71a)
Styrene	*trans*-Stilbene	2.3b)	18a)

a) At 30°C. b) At 0°C.

$1/r_1$ value (k_{12}/k_{11}) is smaller in benzene than in THF, as is shown in Table 4; this suggests that the relative reactivity of a M_2 monomer toward a $\sim\text{St}^-\text{Li}^+$ ion pair is smaller than that toward a styryl free anion, when the reactivities of styrene toward its chain ends are taken as standards.

Chain Transfer and Electronic Spectrum of the Living Anion. The viscosity of the copolymer decreased with an increase in the *trans*-stilbene, as is shown in Table 2. This indicates that a chain transfer to the *trans*-stilbene occurred in THF. This transfer may proceed as follows:



$$\underset{\text{Ph}}{\sim\text{CH}^-} + \overset{\text{Ph}}{\text{CH}}=\underset{\text{Ph}}{\text{CH}} \longrightarrow \underset{\text{Ph}}{\sim\text{CH}_2} + \overset{\text{Ph}}{\text{CH}}=\underset{\text{Ph}}{\text{C}^-} \qquad (4)$$

The production of the anion with a λ_{max} at 555 mμ may be connected with the chain transfer reaction shown by the process (4). On the other hand, the copolymerization in benzene (Table 3) seemed to proceed without the chain transfer, for no change in the red color of the reaction mixture was observed and the solution viscosity of the copolymer did not decrease with an increase in the *trans*-stilbene charged, although the exact molecular weight of the copolymer could not be determined.