BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2659—2663 (1967)

Anionic Copolymerization of Styrene and 1, 1-Diphenylethylene

Heimei YUKI,* Junichi HOTTA,*[1],** Yoshio OKAMOTO* and Shunsuke MURAHASHI**

* *Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka*
** *Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka*

(Received June 17, 1967)

The anionic copolymerization of styrene (M_1) and 1, 1-diphenylethylene (M_2) was investigated. 1, 1-Diphenylethylene, which can not homopolymerize by itself, was copolymerized with styrene by means of an anionic initiator. The copolymerization reaction seemed to proceed without termination or chain transfer, and gave a high molecular alternating copolymer under appropriate reaction conditions. The monomer reactivity ratio, r_1, was obtained from the copolymer composition at the complete consumption of M_1, assuming the rate constant $k_{22}=0$. The monomer reactivity ratio was affected by the solvent (*n*-hexane, benzene, toluene, or THF), but not by the catalyst (*n*-BuLi, Na-dispersion, Na-naphthalene, or K-dispersion) or the reaction temperature. It was 0.4 in toluene at 30°C.

Alternating copolymerization in the radical mechanism has been known with various combinations of monomers, such as styrene and maleic anhydride.[1] On the other hand, the alteranting copolymer had not been obtained by an ionic mechanism until Natta and his co-workers[2] found that the alternating copolymer of ethylene and *cis*-butene-2 could be produced by a Ziegler-type catalyst. Recently they also obtained an alternating copolymer from ethylene and cyclopentene[3] or butadiene[4] with the same type of catalyst.

The present authors have found that, if a suitable combination of monomers was chosen, an alternating copolymer can also be obtained by an anionic mechanism. One of the monomers in the pair was 1, 1-diphenylethylene or *trans*-stilbene; the comonomers used were styrene, butadiene, isoprene, and 2, 3-dimethylbutadiene. The copolymerization had already been reported briefly.[5] Natta *et al.*[6] also reported the alternating copolymerization of 2-vinylpyridine and α-stilbazole by an anionic mechanism.

In the present paper a detailed study of the copolymerization of styrene (M_1) and 1, 1-diphenylethylene (M_2) will be described.

Experimental

Monomer. 1, 1-Diphenylethylene (DPE) was prepared from phenylmagnesium bromide and ethyl acetate.[7] Bp 105—110°C/3—4 mmHg, n_D^{20} 1.6085. Styrene (St) was purified in the usual manner.

Solvent. Benzene, toluene, and *n*-hexane were purified in the usual manner and were dried over metallic sodium. Tetrahydrofuran (THF) was purified, dried over sodium, and distilled from calcium hydride before use.

Catalyst. According to the method of Ziegler[8] *n*-butyllithium (BuLi) was prepared in *n*-heptane, and the concentration (14.9%) was determined by double titration.[9] Sodium dispersion (Na-disp) in *n*-octane and potassium dispersion (K-disp) in *n*-decane were used; the concentrations were 30 and 3% respectively. Sodium naphthalene (Na-Naph) was prepared in tetrahydrofuran; the concentration was 0.3 mmol/m*l*.

Procedure. Copolymerization was carried out in a glass ampoule under nitrogen. Solvent, monomers, and catalyst were placed in the ampoule by using syringes. The ampoule was then allowed to stand in a bath. The reaction was terminated by adding a trace of methanol, and then the contents of the ampoule were poured into a large amount of methanol. The precipitated polymer was separated by filtration, dried, and weighed.

Measurement. The infrared spectrum of the polymer was measured on a Nihon Bunko DS 402G Spectrometer. The conventional KBr method was used for sample preparation. The NMR spectrum of the polymer was obtained in carbon tetrachloride at room temperature with a Varian A60 Spectrometer at 60 Mc/sec. The viscosity was measured in a 1.0 g/d*l* toluene solution at 30.0°C.

[*1] Present address: Mizonokuchi Research Laboratory, Mitsubishi Petrochemical Co., Ltd., Kawasaki, Kanagawa.

1) G. E. Ham, "Copolymerization," Interscience Publishers, New York (1964), p. 747.

2) G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, *J. Am. Chem. Soc.*, **83**, 3343 (1961).

3) G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, *Makromol. Chem.*, **54**, 95 (1962).

4) G. Natta, A. Zambelli, I. Pasquon and F. Ciampelli, *ibid.*, **79**, 161 (1964).

5) H. Yuki, K. Kosai, S. Murahashi and J. Hotta, *J. Polymer Sci. B*, **2**, 1121 (1964).

6) G. Natta, P. Longi and U. Nordio, *Makromol. Chem.*, **83**, 161 (1965).

7) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, p. 226 (1948).

8) K. Ziegler and A. Colonius, *Ann.*, **479**, 135 (1930).

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

Fractionation. The fractionation of the polymer was carried out with a Soxhlet extractor by using diethyl ether or methyl ethyl ketone as the solvent.

Results

The copolymerization by BuLi in toluene was carried out varying the initial molar ratio of styrene to 1, 1-diphenylethylene at 30°C for a prolonged time. The composition of the copolymer was calculated from the ratio of the number of phenyl protons to non-phenyl protons in the NMR spectrum. On the other hand, the composition was also calculated from the polymer yield, assuming that the carbanion of 1, 1-diphenylethylene can not add 1, 1-diphenylethylene; the reaction proceeded sufficiently for the styrene to be completely incorporated into the copolymer. The results are summarized in Table 1.

The polymer yield (weight per cent against the total of monomers charged) decreased with a decrease in the styrene in the initial monomer mixture. The values of the copolymer composition obtained by the two different methods, NMR spectrum and polymer yield, were consistent with each other within the range of experimental error. The composition of the copolymer approached unity when the initial molar ratio of styrene to 1, 1-diphenylethylene was less than unity. The reduced viscosity of the copolymer obtained was around 0.1, but the softening point rose with the increase in the 1, 1-diphenylethylene in the copolymer.

The copolymerization was carried out with BuLi in toluene at 0, 30, and 50°C, equimolar amounts of monomers being used. The results are shown in Table 2. The polymer compositions, St/DPE, were about 1.5; this value seemed to be independent of the reaction temperature. In the copolymerization at 0°C, however, a difference was found between the values calculated by means of the two methods. This must be caused by the styrene remaining unchanged at this temperature, where the reaction rate was rather slow.

The effects of solvent and catalyst in the copolymerization were investigated at 30°C with an equimolar feed composition of monomers. *n*-Hexane, benzene, and toluene were used as solvents,

TABLE 1. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND 1, 1-DIPHENYLETHYLENE (M_2)
—EFFECT OF MONOMER COMPOSITION—
Total monomer 2×10^{-2} mol, solvent: toluene 10 m*l*, temp. 30°C, time 48 hr

St/DPE (mol/mol) in monomer	BuLi (10^{-4} mol)	Yield[a)] %	St/DPE in copolymer from Yield	St/DPE in copolymer from NMR	η_{sp}/C	S.P.[b)] °C	r_1[c)]
∞	5.5	100.0	∞	—	0.09	110	—
2.40	5.5	100.0	2.40	2.45	0.08	145	—
1.57	5.8	98.2	1.62	1.68	0.08	170	0.45
1.04	5.5	86.7	1.32	1.33	0.08	172	0.44
0.92	17.0	84.4	1.21	1.31	—	117	0.35
0.67	4.4	71.4	1.13	0.96	0.11	175	0.30
0.69	8.2	70.5	1.19	0.93	0.07	140	0.41
0.33	5.8	45.1	0.97	—	—	165	—
0.17	5.8	24.6	0.95	1.00	—	158	—

a) Wt% against total monomer.
b) Softening point.
c) Calculated from the copolymer composition obtained from polymer yield.

TABLE 2. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND 1, 1-DIPHENYLETHYLENE (M_2)
—EFFECT OF TEMPERATURE—
Total monomer 2×10^{-2} mol, solvent: toluene 10 m*l*, time 48 hr

Temp. °C	St/DPE (mol/mol) in monomer	BuLi 10^{-4} mol	Yield %	St/DPE in copolymer from Yield	St/DPE in copolymer from NMR	η_{sp}/C	S.P.[a)] (°C)	r_1[b)]
0	1.00	5.6	68.3	2.02[c)]	1.32	0.12	171	0.47[d)]
30	1.04	5.5	86.7	1.32	1.33	0.08	172	0.44
50	1.10	5.3	87.3	1.40	1.25	0.09	169	0.55

a) Softening point.
b) Calculated from the copolymer composition obtained from polymer yield.
c) Reaction did not proceed completely.
d) Calculated from the copolymer composition obtained from NMR.

TABLE 3. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND 1, 1-DIPHENYLETHYLENE (M_2)
—EFFECTS OF SOLVENT AND CATALYST—
Total monomer 2×10^{-2} mol, temp. 30°C, solvent 10 m*l*

St/DPE (mol/mol) in monomer	Solvent	Catalyst	(10^{-4} mol)	Time hr	Yield %	St/DPE in copolymer		η_{sp}/C	r_1 b)
						from Yield	from NMR		
1.02	THF	BuLi	4.0	48	95.1	1.11	1.04	0.11	0.13
1.10	THF	Na-Naph	1.2×10	48	97.6	1.14	1.19	0.11	0.14
0.99	THF	Na-disp	3.1×10	48	88.5	1.21	—	0.18	0.29
1.00	THF	K-disp	7.2	48	90.5	1.18	—	0.31	0.23
1.04	Toluene	BuLi	5.5	48	86.7	1.32	1.33	0.08	0.44
0.96	Toluene	Na-disp	6.2×10	96	73.7a)	1.62	1.83	0.08	—
0.93	Toluene	K-disp	1.1×10	96	83.4a)	1.25	1.06	0.15	—
0.93	Benzene	BuLi	8.0	72	77.8	1.40	1.35	0.16	0.71
0.97	Benzene	Na-disp	2.2×10^2	96	62.5a)	2.32	0.98	0.21	—
0.97	Benzene	K-disp	9.5	96	74.4a)	1.68	1.14	0.35	—
1.03	Hexane	BuLi	4.0	72	80.8a)	1.38	1.40	—	0.63
0.98	Hexane	Na-disp	1.9×10^2	72	30.1a)	—	1.30	0.39	—

a) Reaction proceeded in heterogeneous system.
b) Calculated from the copolymer composition obtained from polymer yield.

TABLE 4. ANIONIC COPOLYMERIZATION OF STYRENE (M_1) AND 1, 1-DIPHENYLETHYLENE (M_2)
Solvent THF, catalyst BuLi, temp. 0°C

Monomers 10^{-2} mol	St/DPE (mol/mol) in monomer	BuLi 10^{-4} mol	Monomers/BuLi	Time hr	Yield %	Copolymer		
						St/DPE	η_{sp}/C a)	S.P.
4.42	∞	0.72	610	0.5	100	∞	0.85	160
42.54	13.5	2.57	1650	24	100	13.5	2.21	180
11.14	3.71	1.14	980	24	98	3.7	0.77	180
19.20	2.74	1.14	1690	48	99	2.7	1.76	180
12.32b)	0.72	1.14	1080	144	56	1.0c)	1.08	245

a) Benzene solution, $c=1.0$ g/d*l*, at 30.0°C
b) Styrene was added every six hours dividing into four portions.
c) Obtained from NMR.

and BuLi, Na-dispersion, K-dispersion, and Na-naphthalene, as catalysts. Table 3 shows the results. Depending on the solvent and catalyst used, the reaction mixture formed a homogeneous or heterogeneous system. The heterogeneity of system decreased with an increase in the polarity of the reaction mixture. The homogeneous system generally gave the copolymer in a good yield, but the heterogeneous one resulted in a low yield. In THF, the reaction proceeded in a homogeneous system independently of the catalyst used, and the values of copolymer composition calculated by the two methods showed a good coincidence. When the reaction proceeded in a heterogeneous system, some discrepancy was observed between the values of copolymer composition calculated from the polymer yield and from the NMR spectrum. In this case the reaction did not proceed completely, both the monomers remaining unchanged.

The monomer reactivity ratio, r_1, in the copolymerization of styrene (M_1) and 1, 1-diphenylethylene (M_2) was calculated from the copolymer composition by using Eq. (9), which will be described in the next section. The values of r_1 obtained are listed in Tables 1, 2, and 3. As a mean value 0.4 was obtained for r_1 in the copolymerization carried out with BuLi in toluene. This value seemed to be independent of the initial molar ratio of monomers (Table 1) and of the reaction temperature from 0 to 50°C (Table 2).

It was found that the monomer reactivity ratio, r_1, was affected by the nature of the solvent; *i. e.*, the value was smaller in a polar solvent, and the relative reactivity of styrene appeared to increase in a non-polar solvent (Table 3). Little effect on r_1 was observed with the catalyst.

The copolymerization with BuLi was carried out in THF at 0°C. In this reaction the amount of catalyst was minimized in order to obtain a large molecular weight of the polymer. The results are shown in Table 4. In the copolymerization when the initial molar ratio of styrene to 1, 1-diphenylethylene was large enough, the copolymer was obtained quantitatively after 48 hours. However, when the ratio was less than unity, the reaction proceeded slowly, unchanged styrene existing

TABLE 5. FRACTIONATION OF COPOLYMER

Polymerization		Original polymer		Insoluble polymer a)			
Solvent	Catalyst	St/DPE	η_{sp}/C	Solvent b)	%	St/DPE	η_{sp}/C
Toluene	BuLi	1.33	0.08	Et_2O	74	1.33	—
Benzene	K-disp	1.14	0.35	MEK	69	1.00	0.38
THF	K-disp	0.95	0.31	MEK	71	1.04	0.38
THF	BuLi	0.96	—	Et_2O	88	1.04	—
THF	BuLi	3.70	0.77	MEK	0	—	—
				Et_2O	100	3.70	0.77
				Acetone	100	3.70	0.77
THF	BuLi	1.00	1.08	MEK	100	1.00	1.08
				Et_2O	100	1.00	1.08

a) After extraction for 10 hr.

b) Et_2O: diethyl ether, MEK: methyl ethyl ketone.

even after 6 days. The polymer viscosity increased with an increase in the initial ratio of the total quantity of monomers to that of BuLi. Probably the copolymerization proceeded in a living system and no chain transfer occurred, although it was impossible to compare the molecular weights of copolymers possessing different compositions. The softening point of the copolymer rose with the increase in the amount of 1, 1-diphenylethylene in the copolymer.

In order to obtain more information about the homogeneity of the copolymer with regard to its composition and molecular weight, some of the copolymers were fractionated by extraction. The results (Table 5) showed that the copolymer rich in styrene is soluble in methyl ethyl ketone, even at a high molecular weight, but was insoluble in both diethyl ether and acetone, while the alternating copolymer with a high molecular weight is not soluble in methyl ethyl ketone. It was found that the lower-molecular-weight polymers had contained some soluble fractions in diethyl ether or methyl ethyl ketone. However, only small changes in the copolymer composition and viscosity were observed in the insoluble fractions. In these cases the original polymers were obtained by a heterogeneous catalyst or at higher catalyst concentrations; thus they contained lower molecular-weight fractions, for the initiation reaction did not take place at once. In general, the copolymers produced in these copolymerization have been shown to be essentially homogeneous.

Discussion

Evans and his co-workers have reported that in benzene *n*-butyllithium adds rather faster to 1, 1-diphenylethylene than to styrene,10) and that the former olefin can dimerize but not polymerize to a higher polymer,11) probably because of the steric hindrance due to the second phenyl group in the 1, 1-diphenylethylene. From thier experimental results, even the dimerization of 1, 1-diphenylethylene seems not to be so fast, because 1, 1-diphenylhexane, the addition product of *n*-butyllithium and 1 mole of 1, 1-diphenylethylene, remained in the reaction mixture after the reaction. The higher reactivity of 1, 1-diphenylethylene to the carbanion than that of styrene may be interpreted by the resonance stabilization of the 1, 1-diphenylethylene anion being larger than that of the styryl anion. These results suggest that, in the copolymerization of 1, 1-diphenylethylene and styrene, the styryl anion may add faster to 1, 1-diphenylethylene than to styrene, and that the 1, 1-diphenylethylene anion adds more easily to styrene than to 1, 1-diphenylethylene. Thus, the reaction may lead to the production of an alternating colymer of these two monomers. Strictly speaking, in the following copolymerization reactions:

$$\sim\!\sim M_1^- + M_1 \xrightarrow{k_{11}} \sim\!\sim M_1M_1^- \qquad (1)$$

$$\sim\!\sim M_1^- + M_2 \xrightarrow{k_{12}} \sim\!\sim M_1M_2^- \qquad (2)$$

$$\sim\!\sim M_2^- + M_1 \xrightarrow{k_{21}} \sim\!\sim M_2M_1^- \qquad (3)$$

$$\sim\!\sim M_2^- + M_2 \xrightarrow{k_{22}} \sim\!\sim M_2M_2^- \qquad (4)$$

if the rate constant, k_{22}, is small enough, and if k_{12} is sufficiently larger than k_{11}, the crossover propagation must occur predominantly and result in an alternating copolymer at $(M_2)_0/(M_1)_0>1$, where (M_2) and (M_1) are the concentrations of M_2 and M_1 respectively.

As shown in Table 1, this situation held in the copolymerization of 1, 1-diphenylethylene and styrene. The coincidence of the copolymer composition obtained by NMR spectroscopy and that calculated from the polymer yield at a complete consumption of the monomer M_1 suggests the

---

10) A. G. Evans and D. B. George, *J. Chem. Soc.*, **1961**, 4653.

11) A. G. Evans and D. B. George, *ibid.*, **1962**, 141.

validity of the assumption that $k_{22}=0$, which indicates that not even a dimeric unit of the monomer M_2 exists in the copolymer.

In the copolymerization of M_1 and M_2, if the M_2 anion does not add M_2, that is, if $k_{22}=0$, the copolymer composition equation reduces to:

$$\frac{d(M_1)}{d(M_2)} = r_1 \frac{(M_1)}{(M_2)} + 1 \tag{5}$$

On the other hand, the next equation is deduced easily:

$$\frac{d(M_1)/(M_2)}{d(M_2)} = -\frac{(M_1)}{(M_2)^2} + \frac{1}{(M_2)} \cdot \frac{d(M_1)}{d(M_2)} \tag{6}$$

Substituting (5) into (6), we have:

$$\frac{d(M_1)/(M_2)}{d(M_2)} = \frac{1}{(M_2)}\left(r_1 \frac{(M_1)}{(M_2)} - \frac{(M_1)}{(M_2)} + 1\right) \tag{7}$$

The integration of Eq. (7) gives:

$$\ln \frac{(M_2)}{(M_2)_0} + \frac{1}{r_1-1} \ln \frac{[(M_1)/(M_2)](r_1-1)+1}{[(M_1)_0/(M_2)_0](r_1-1)+1} = 0 \tag{8}$$

where $r_1 \neq 1$ and where $(M_1)_0$ and $(M_2)_0$, and (M_1) and (M_2), represent the initial and final monomer concentrations respectively. When unchanged M_1 does not exist in the copolymerization system, *i. e.*, when $(M_1)=0$, we have:

$$\ln \frac{(M_2)}{(M_2)_0} + \frac{1}{r_1-1} \ln \left[\frac{(M_1)_0}{(M_2)_0}(r_1-1) + 1\right] = 0 \tag{9}$$

Equation (9) gives r_1 when $(M_1)_0$, $(M_2)_0$, and (M_2) are known.

As Table 1 shows, r_1 was found to be 0.30—0.45 (mean value=0.4) in toluene at 30°C at a variety of $(M_2)_0/(M_1)_0$ ratios. The reaction temperature and the species of counter ion seemed not to affect the reactivity ratio, while an influence of the solvent used for the reaction was apparent; *i. e.*, the r_1 value increased with a decrease in the polarity of the solvent. The cause of this change in the reactivity ratio is not certain at the present time, but it seems to concern the degree of dissociation of the ion-pair to the free ions in the solution.

Szwarc *et al.*[12)] have reported the anionic copolymerization of styrene and 1, 1-diphenylethylene by Na in THF at 25°C. From their kinetic study they obtained the rate constants, k_{12}, for the ion-pair (250 l/mol sec) and the free ion (400000 l/mol sec), and the apparent rate constant, k_{21} (0.5—0.7 l/mol sec). They concluded that the step (3) in the above equations is reversible (the equilibrium constant $K_{21}=5\times10^{-2}$ l/mol) and rate determining, while the reaction (2) is very fast and prevents the reaction (1). The monomer reactivity ratio, r_1, in THF at 25°C with the Na^+ counter ion can be calculated as 0.21 from Szwarc's data ($k_{11}=210$ l/mol sec and $k_{12}=1000$ l/mol·sec),[12,13)] which represent the apparent rate constants at the same concentration of the living end (0.04 mol/l) as that employed in the present work. The value shows a good agreement with the 0.2 obtained in the present copolymerization in THF with Na.

The reduced copolymer composition equation, (5), suggests that if the initial molar ratio of monomers $(M_1)_0/(M_2)_0$ is $1/(1-r_1)$, where $r_1<1$, *i. e.*, $k_{11}<k_{12}$, the copolymerization proceeds azeotropically. At $(M_1)_0/(M_2)_0>1/(1-r_1)$, both the monomers can be consumed completely by the copolymerization, and so the copolymer composition must be the same with the monomers fed. However, in this case the monomers react alternatingly in the initial stage, with M_1 remaining predominantly and with this incorporated in the copolymer more and more in the later stage. As we can expect, from the chemical structures of styrene and 1, 1-diphenylethylene, that neither termination nor chain transfer occurs in this copolymerization, the polymer molecule obtained must have a constitution obeying this change in reaction. At $(M_1)_0/(M_2)_0<1/(1-r_1)$, an essentially alternating copolymerization proceeds, but the deviation takes place at the initial stage and a more strict alternating condition is reached at the final stage, the monomer M_2 remaining unchanged.

From the results of fractionation, it may be concluded that the high-molecular-weight polymer produced in the copolymerization with a careful procedure included no low molecular fraction, and that probably there was also no fraction with a composition deviating greatly from that to be anticipated from the amounts of charged monomers.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

---

12) E. Ureta, J. Smid and M. Szwarc, *J. Polymer Sci. A-1*, **4**, 2219 (1966).

13) D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).