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Reactivity of n-Butyllithium–$CH_3OCH_2CH_2OLi$ System as Catalyst for Copolymerization of Styrene with 1,3-Butadiene

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SUMMARY

The reactivity of n-butyllithium-$CH_3OCH_2CH_2OLi$ in toluene (System A) in styrene-butadiene copolymerization reaction was found to be similar to that of the catalyst system n-butyllithium-poly(propylene oxide), which formed copolymers containing more styrene units than the feed monomer ratio at early stage of polymerization. Metalation reaction of toluene to produce benzyllithium was observed to take place in System A. Relative reactivity of each of chemical species present in System A was measured in the reactions with butadiene, styrene, and 1,1-diphenylethylene, in connection with initiation and propagation reactions of copolymerization. From this study a living end anion possessing larger conjugated system was concluded to be more reactive toward monomers possessing larger conjugated system.

INTRODUCTION

Many studies on anionic polymerizations of styrene and butadiene have been reported. The rate of homopolymerization of styrene initiated with n-butyllithium (n-C_4H_9Li) in hydrocarbons such as toluene and cyclohexane is known to be greater than that of butadiene. However, when these monomers are copolymerized under the same conditions, butadiene is incorporated more rapidly at the initial stage of the copolymerization reaction. Styrene is not copolymerized significantly until butadiene concentration in monomer phase is much lowered, copolymers formed here being known to possess a block-type structure [1].

According to kinetic studies of Worsfold [2] and Morton [3], the end group of the growing polymer is mostly butadiene anion because styrene anion reacts very rapidly with butadiene.

When a small amount of a polar compound (tetrahydrofuran, diethyl ether, triethylamine, etc.) is added to this copolymerization system, the reactivity of styrene at the initial stage increases to form random copolymers. By use of the polar compounds mentioned above, however, the enhancement of styrene reactivity is not brought about to an extent which results in formation of copolymers containing more styrene units than the feed monomer ratios [1, 4].

Narita and Tsuruta recently reported the effects of polyethers, such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), on the reactivity of n-C_4H_9Li in the copolymerization reaction of styrene and butadiene [5]. The copolymer obtained by the n-C_4H_9Li-polyether system was found to contain more styrene units than feed monomer ratio when mole ratio of ether oxygen and n-C_4H_9Li ([–O–]/[Li] was between 1.5 and 2.0.

Poly(ethylene oxide) was reported by Vandenberg [6] to react with a small quantity of n-C_4H_9Li ([–O–]/[Li]) = 50 - 100) under the scission of its main chain in the following way:

$$-OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2- + n\text{-}C_4H_9Li$$

$$\longrightarrow -OCH_2CH_2OCH{=}CH_2 + LiOCH_2CH_2OCH_2- + n\text{-}C_4H_{10}$$

Under conditions adopted by Vandenberg, C–Li linkages were completely converted to O–Li. In our system the relative amount of polyether was much smaller than in the case of Vandenberg; for example, [–O–]/[Li] ratio in n-C_4H_9Li-PEO catalyst system was between 1.5 and 2.0. In this system, in contrast with the Vandenberg study, about 30% of C–Li linkages was found to survive and PEO was cleaved, producing large amount of alcoholate having the general structure CH_2=$CH(OCH_2CH_2)_nOLi$ ($n \geqq 1$). This type of alcoholate was considered to form the catalyst species in toluene with surviving n-C_4H_9Li [5].

On the basis of the above observation, we studied the catalyst system of n-C_4H_9Li associated with $ROCH_2CH_2OLi$, one of model compounds of CH_2=$CH(OCH_2CH_2)_nOLi$ [5]. When the [OLi]/[CLi] ratio was 2.0, the copolymer obtained at the initial stage of copolymerization reaction was found to contain more styrene units than the feed monomer ratio, a fact which was similar to the case of the n-C_4H_9Li-PPO (or PEO) system.

This paper presents the results of a study on chemical behaviors of n-C_4H_9 Li-$CH_3OCH_2CH_2OLi$ *catalyst system in toluene (System* A) and in cyclohexane, where 1) metalation reaction in System A to produce benzyllithium ($C_6H_5CH_2Li$) was examined; and 2) the reactivity of System A to 1,1-diphenylethylene, styrene, and butadiene was measured to get a hint on explaining the increased reactivity of styrene in the styrene-butadiene copolymerization in connection with initiation and propagation reaction mechanisms.

EXPERIMENTAL

Reagents

Benzene, toluene, and cyclohexane were purified by the usual method under purified nitrogen. Ethylene glycol monomethyl ether (methyl cellosolve) was refluxed over CaH_2 and distilled. n-C_4H_9Li was prepared from n-C_4H_9Cl and Li metal in purified petroleum ether under nitrogen [7]. Ethyllithium was prepared from C_2H_5Br and Li dispersion. $C_6H_5CH_2Li$ was prepared in hydrocarbon media according to the literature [8]. 1,1-Diphenylethylene was synthesized by the usual method [9]. Styrene and butadiene were purified under nitrogen by the usual method. Dimethyl sulfate was distilled under reduced pressure; bp 66°C (8 mm Hg).

Styrene-Butadiene Copolymerization Reaction [5]

Catalyst solutions were prepared in toluene or in cyclohexane beforehand. The copolymerizations were carried out in glass ampules under a nitrogen atmosphere at 40°C. After a certain period the reaction mixture was poured in methanol containing a small amount of phenyl-β-naphthylamine as antioxidant. Methanol insoluble product was dried in vacuo at 40°C. The double bonds of the butadiene units involved in copolymers obtained were analyzed by the ICl titration method [10], and from this the styrene content was calculated.

Metalation Reaction of Toluene

A toluene solution of n-C_4H_9Li was added by a syringe into a magnetically stirred solution of $CH_3OCH_2CH_2OLi$ in toluene under nitrogen. Dimethyl sulfate was added after standing 30 min at room temperature, and methylation products (n-pentane and ethylbenzene) were quantitatively analyzed by vapor-phase chromatography (VPC). Nuclear magnetic resonance (NMR) spectra at 60 Mc were measured with a Japan Electron Optics Laboratory C-60 spectrometer.

Relative Reactivity of System A to 1,1-Diphenylethylene, Styrene, and Butadiene

1,1-Diphenylethylene, styrene, or butadiene was added to System A. The reaction was quenched after various time intervals by sampling a portion of the solution and adding it to dimethyl sulfate. The methylation products were analyzed by VPC.

Identification of Reaction Products of System A with 1,1-Diphenylethylene

1,1-Diphenylethylene was added to System A. Red precipitates and the supernatant solution were separated and each was hydrolyzed. The products were separated by column chromatography with a 13-cm activated alumina column and n-hexane as developing solvent.

Elemental analysis: for reaction product $CH_3(CH_2)_4CH(C_6H_5)_2$, Calc. C% 90.7, H% 9.31; found C% 90.4, H% 8.95; for reaction product $C_6H_5CH_2CH_2CH(C_6H_5)_2$, calc. C% 92.7, H% 7.29; found C% 92.0, H% 7.36.

RESULTS AND DISCUSSION

Styrene-Butadiene Copolymerization Reaction in Toluene

Results of styrene-butadiene copolymerization reactions with n-C_4H_9Li and some ethers in toluene are cited in Table 1 [5].

Copolymers obtained with n-C_4H_9Li-PPO systems contain more styrene units than feed monomer ratio (3:7). Since the styrene content shows only a small change up to 40% conversion, the copolymers are considered to

Table 1. Copolymerization between Styrene and Butadiene with n-C_4H_9Li–Ether Systems[a]

Ether	$\frac{[OLi]}{[CLi]}$	Polymerization time (min)	Conversion (mole %)	Styrene content (mole %)
PPO	–[b]	60	10.8	51.4
		120	17.4	48.6
		180	22.3	50.6
		240	32.4	48.5
		300	39.2	41.8
$CH_2=CHOCH_2CH_2OLi$[c]	2.0	225	17.4	32.6
$CH_3OCH_2CH_2OLi$	1.0	30	42.1	33.9
	1.0	60	82.4	34.3
	2.0	4	53.8	50.5

[a] Polymerization conditions: styrene 27 mmole, butadiene 63 mmole, n-C_4H_9Li 0.9 mmole, toluene 15 ml, polymerization temp., 40°C.

[b] $[-O-]/[Li] = 1.5$.

[c] Styrene 24.6 mmole, butadiene 57.8 mmole, n-C_4H_9Li 0.82 mmole, n-$C_6H_{13}OLi$ 4.92 mmole, $CH_2=CHOCH_2CH_2OLi$ 1.64 mmole, polymerization temp., 40°C.

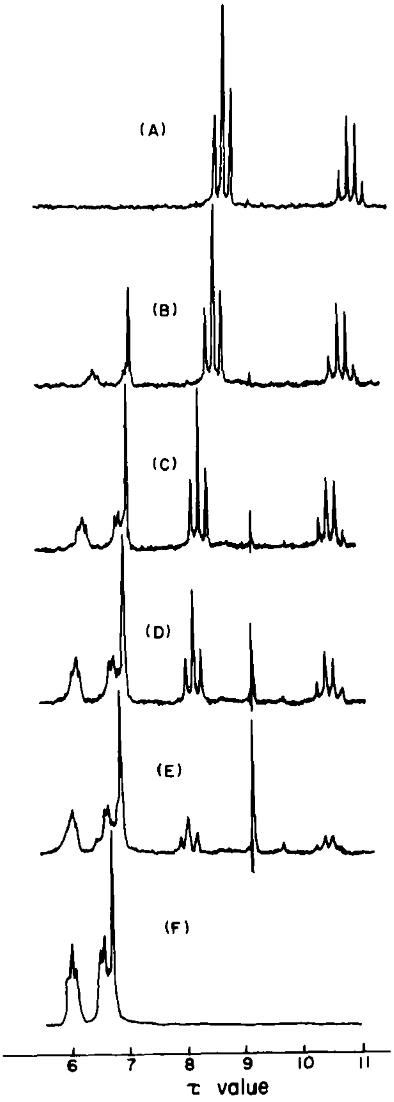

Fig. 1. NMR spectra of CH_3CH_2Li–$CH_3OCH_2CH_2OLi$ system in benzene: (A) CH_3CH_2Li, (B) [OLi]/[CLi] = 0.2, (C) [OLi]/[CLi] = 0.4, (D) [OLi]/[CLi] = 1.0, (E) [OLi]/[CLi] = 1.4, and (F) $CH_3OCH_2CH_2OLi$.

possess a high degree of randomness. The average for butadiene stereochemistry is 70% 1,2- and 30% 1,4-trans structure. The styrene content of copolymers in the range of [—O—]/[Li] below 1 were found to be much the same as those obtained with n-C_4H_9Li alone in hydrocarbon media.

The catalyst system of n-C_4H_9Li and $CH_2{=}CHOCH_2CH_2OLi$ also gives a copolymer containing more than 30% styrene units. Since $CH_2{=}CHOCH_2CH_2OLi$ was previously found in the reaction system of n-C_4H_9Li and PEO ([—O—]/[Li] = 1.5 - 2.0) to be formed in quantity, the data in Table 1 suggest that $CH_2{=}CHOCH_2CH_2OLi$ is responsible for the formation of active species of the n-C_4H_9Li-PEO system. When another model compound, $CH_3OCH_2CH_2OLi$, is added to copolymerization system, the copolymers formed also contain more styrene units than the feed monomer ratio.

NMR Spectra of RLi-$CH_3OCH_2CH_2OLi$ in Benzene

As described above, the n-C_4H_9Li-$R'OCH_2CH_2OLi$ catalyst system exhibited a peculiar behavior in styrene-butadiene copolymerization, the structure and reactivity of the catalyst system being of interest in connection with initiation and propagation reactions.

Figure 1 shows the NMR spectra of the ethyllithium-$CH_3OCH_2CH_2OLi$ system in benzene. Signals of CH_2Li and $CH_3OCH_2CH_2OLi$ become broader with an increase in [OLi]/[CLi] values. This suggests that C_2H_5Li and $CH_3OCH_2CH_2OLi$ form complexes which have rather rigid structures. A peak derived from ethane appears at τ 9.2, the intensity of which increases with an increase in [OLi]/[CLi] values. Ethane comes from a metalation reaction of benzene with C_2H_5Li.

Metalation reaction was confirmed by a reaction of n-C_4H_9Li–$CH_3OCH_2CH_2OLi$ in benzene with carbon dioxide. After the carbonation mixture was hydrolyzed, the formation of benzoic acid along with valeric acid was identified. Since toluene is used as the solvent for the copolymerization, metalation reactions of toluene will be examined in more detail.

Metalation Reaction of Toluene with n-C_4H_9Li-$CH_3OCH_2CH_2OLi$ System

The metalation reaction of toluene is considered to proceed in the following way:

$$C_6H_5CH_3 + n\text{-}C_4H_9Li \longrightarrow C_6H_5CH_2Li + n\text{-}C_4H_{10} \qquad (1)$$

When the reaction systems are treated with dimethyl sulfate, $C_6H_5CH_2Li$

Table 2. Metalation Reaction of Toluene with n-C_4H_9Li-$CH_3OCH_2CH_2OLi$ System[a]

$\frac{[OLi]}{[CLi]}$	n-Pentane (mole %)	Ethylbenzene (mole %)
0.5	95	0
1.0	87	13
1.5	79	21
2.0	37	56

[a] Reaction conditions: n-C_4H_9Li 5.65 mole, toluene 10 ml., reaction temp., room temp., reaction time 30 min., dimethyl sulfate (methylating agent) 1 ml.

and n-C_4H_9Li are converted to ethylbenzene and n-pentane, respectively. The results of measurements on each compound present in the reaction systems with various [OLi]/[CLi] ratios are summarized in Table 2.

Figure 2 shows the temperature dependence of the metalation reaction. The metalation reaction is considered to proceed in such a way that some parts of n-C_4H_9Li aggregates are loosened by $CH_3OCH_2CH_2OLi$, resulting in the formation of a complex, n-C_4H_9Li-$CH_3OCH_2CH_2OLi$, which is able to liberate an active anion and abstract a proton from toluene to leave benzyllithium complexed with $CH_3OCH_2CH_2OLi$.

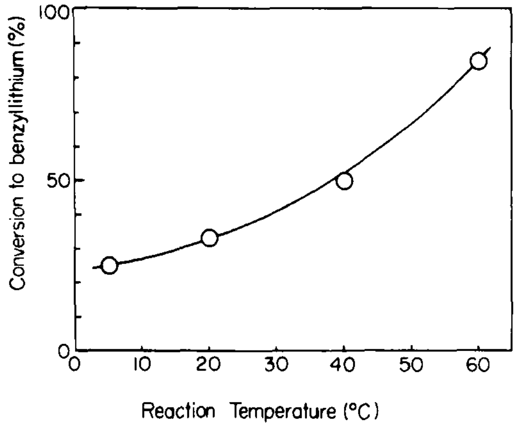

Fig. 2. Temperature dependence of metalation reaction. Cf. Table 2.

Lithium 2-dimethylaminoethanolate, $(CH_3)_2NCH_2CH_2OLi$, was found to behave in a similar way to $CH_3OCH_2CH_2OLi$ [11].

The metalation reaction in System A proceeds in a homogeneous phase, but the yield is rather low compared with N,N,N′,N′-tetramethylethylenediamine (TMEDA)-n-C_4H_9Li system in toluene [12-15]. Ring metalation of toluene is not detected in System A, in contrast with system TMEDA-n-C_4H_9Li where the ring metalation was reported to occur at about 10% [12]. As mentioned in the last section, none of possible products, such as $CH_3C_6H_4CH_2CH(C_6H_5)_2$, which may result from the participation of ring metalation compounds, can be detected.

Since System A is formed from three components, n-C_4H_9Li, $C_6H_5CH_2Li$, and $CH_3OCH_2CH_2OLi$ as mentioned above, elucidation of the chemical behavior of System A should be made in terms of the reactivities of n-C_4H_9Li and $C_6H_5CH_2Li$ with and without complexing with $CH_3OCH_2CH_2OLi$, which will be discussed in the following sections.

Styrene-Butadiene Copolymerization Reaction in Cyclohexane

Direct information of the nature of the n-C_4H_9Li-$CH_3OCH_2CH_2OLi$ system can be obtained when styrene and butadiene are copolymerized in cyclohexane, because n-C_4H_9Li is the only organolithium compound in the cyclohexane system. The results obtained are shown in Table 3.

Table 3. Copolymerization of Styrene and Butadiene by n-C_4H_9Li-$CH_3OCH_2CH_2OLi$ System in Cyclohexane[a]

$\frac{[OLi]}{[CLi]}$	Polymerization time (min)	Conversion (mole %)	Styrene content (mole %)
0	50	46.2	7.7
0.5	60	52.9	9.8
1.0	5	40.3	33.6
1.0	7	70.2	32.1
2.0[b]	5	39.6	69.6

[a] Polymerization conditions: styrene 27 mmole, butadiene 63 mmole, n-C_4H_9Li 0.9 mmole, cyclohexane 15 ml., polymerization temp., 40°C.

[b] Styrene 10.5 mmole, butadiene 24.5 mmole, n-C_4H_9Li 0.35 mmole, cyclohexane 60 ml., polymerization temp., 40°C.

It was found again that copolymers obtained by catalyst systems with [OLi]/[CLi] = 1.0 and 2.0 possess more styrene units than the feed monomer ratio (3:7) when the copolymerization reactions are terminated at about 50% conversion. On the other hand, the presence of less than 0.5 mole $CH_3OCH_2CH_2OLi$ with respect to n-C_4H_9Li has no effect on the copolymer composition.

These results indicate that $C_6H_5CH_2Li$ is not indispensable for formation of copolymers containing more styrene units than the feed monomer ratio.

Styrene-Butadiene Copolymerization with $C_6H_5CH_2Li$—$CH_3OCH_2CH_2OLi$ System

The presence of $C_6H_5CH_2Li$ in System A required that we examine the reactivity of $C_6H_5CH_2Li$ itself in the copolymerization reaction. Contrary to n-butyl anion, benzyl anion consists of a large frame work of conjugated system. The more stable anion was suspected to cause some enhancement of styrene reactivity even in the absence of $CH_3OCH_2CH_2OLi$. Results obtained from examination on the possibility of enhancing effect of $C_6H_5CH_2Li$ itself for styrene reactivity are shown in Table 4.

Table 4. Copolymerization of Styrene and Butadiene with $C_6H_5CH_2Li$-$CH_3OCH_2CH_2OLi$ System in Toluene[a]

$\frac{[OLi]}{[CLi]}$	Polymerization time (min)	Conversion (mole %)	Styrene content (mole %)
0	40	45.3	9.1
2.0	3	41.7	54.0
2.0	7	78.0	42.0

[a]Polymerization conditions: styrene 16.9 mmole, butadiene 39.4 mmole, $C_6H_5CH_2Li$ 0.563 mmole, toluene 20 ml., polymerization temp., 40°C.

Table 4 shows that $C_6H_5CH_2Li$ behaves similarly to n-C_4H_9Li in the styrene-butadiene copolymerization.

Reactivity of System A with 1,1-Diphenylethylene, Styrene, and Butadiene

The reactivity of System A with styrene and butadiene is discussed in this section in connection with the initiation and propagation reactions of copolymerization. 1,1-Diphenylethylene was also used as a reactant because it has a larger conjugated system than styrene. The monomer reactivity in the copolymerization with System A seemed to depend largely on differences in size of the conjugation frame work of monomer molecules. It was anticipated that the behavior of 1,1-diphenylethylene would yield information about changes in the character of System A. 1,1-Diphenylethylene also has the merit that addition products of the initiation reaction can be separated and identified because this monomer does not homopolymerize. The reaction mode of System A with 1,1-diphenylethylene is discussed in detail in the next section.

Table 5 shows the changed organolithium compound percent in System A on reacting with the three monomers. The calculation is based on the initial concentration of each organolithium compound.

All the monomers react more rapidly with each organolithium compound in System A than with n-C_4H_9Li alone.

The addition reaction of 1,1-diphenylethylene with n-C_4H_9Li in the absence of $CH_3OCH_2CH_2OLi$ takes place only with difficulty, but n-C_4H_9Li in System A can react much more rapidly. $C_6H_5CH_2Li$ in System A exhibits the greatest reactivity toward 1,1-diphenylethylene: it is consumed completely within 1 min.

Styrene is consumed completely immediately after the reaction starts because the propagation reaction is very fast. It may safely be said, however, that $C_6H_5CH_2Li$ in System A is the most reactive and that n-C_4H_9Li associated with $CH_3OCH_2CH_2OLi$ is more reactive than n-C_4H_9Li alone.

In reactions with butadiene, n-C_4H_9Li in System A is the most reactive. It may be noted that the reactivities of $C_6H_5CH_2Li$ in System A and n-C_4H_9Li in the absence of $CH_3OCH_2CH_2OLi$ are not much different from each other, contrary to cases with styrene and 1,1-diphenylethylene.

From Table 5 it can be asserted that the larger conjugated monomer molecule reacts more rapidly with $C_6H_5CH_2Li$ in System A (conjugated anion) as shown clearly in the reaction with 1,1-diphenylethylene. Although styrene molecule possesses a smaller conjugated system than 1,1-diphenylethylene, the behavior of the former is considered to be similar to that of the latter. The changed organolithium compounds with styrene in System A do not go beyond about 35 and 60%, respectively, which is interpreted in terms of the rapid consumption of the monomer molecules owing to the great propagation speed.

On the basis of results in Table 5, the increasing reactivity of styrene in the copolymerization will be explained as follows. With the use

Table 5. Reactions of 1,1-Diphenylethylene, Styrene, and Butadiene with System A[a]

Monomer	Reaction time (min)	Changed organolithium compound (%)		
		n-C_4H_9Li in the absence of $CH_3OCH_2CH_2OLi$	n-C_4H_9Li in System A	$C_6H_5CH_2Li$ in System A
$CH_2{=}C(C_6H_5)_2$[b]	0.5	–	–	94
	1	–	33	100
	3	–	48	100
	5	–	54	100
	7	8	65	100
$CH_2{=}CHC_6H_5$[b]	1	~25	~37	~62
	3	~25	~37	~60
	5	~28	~33	~61
$CH_2{=}CH{-}CH{=}CH_2$[c]	1	36	63	29
	3	40	81	38
	6	45	87	61

[a] Reaction conditions: [OLi]/[CLi] = 2.0, reaction temp., 20°C.

[b] [Monomer] 1.25 mole/1; [CLi] 0.113 mole/1.

[c] [Monomer] 0.89 mole/1; [CLi] 0.080 mole/1.

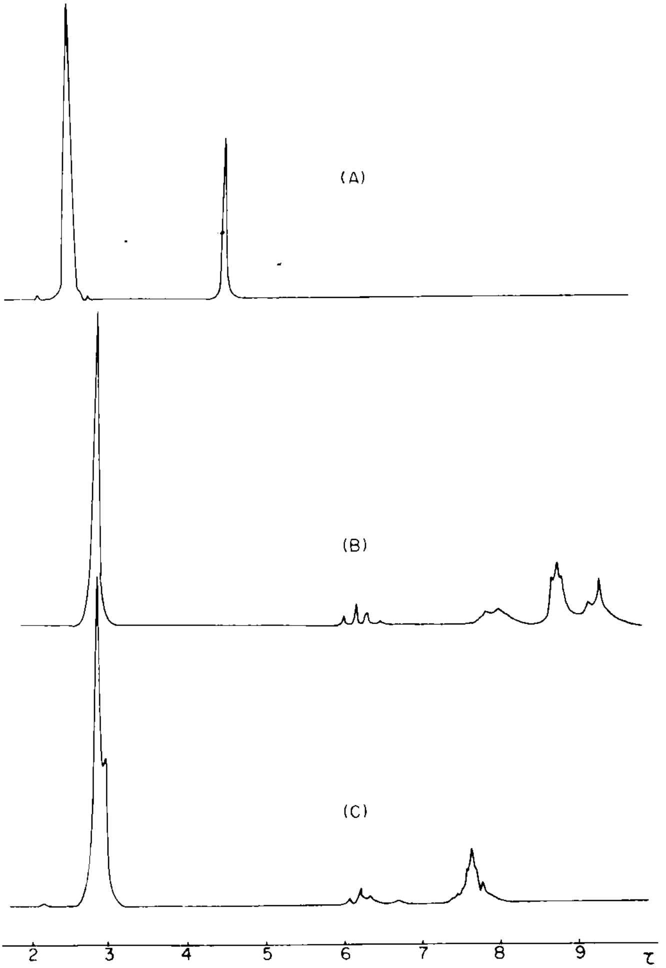

Fig. 3. NMR spectra of 1,1-diphenylethylene (A), 1,1-diphenylhexane (B), and 1,1,3-triphenylpropane (C).

of n-C_4H_9Li in the absence of $CH_3OCH_2CH_2OLi$, the reactivity order of the monomer is butadiene > styrene > 1,1-diphenylethylene.

Therefore, in the copolymerization reaction between styrene and butadiene with n-C_4H_9Li in toluene butadiene anion is formed in much larger amount at the initiation step. Most of butadiene anions react rapidly with butadiene monomer. Even when butadiene anion happens to react, by

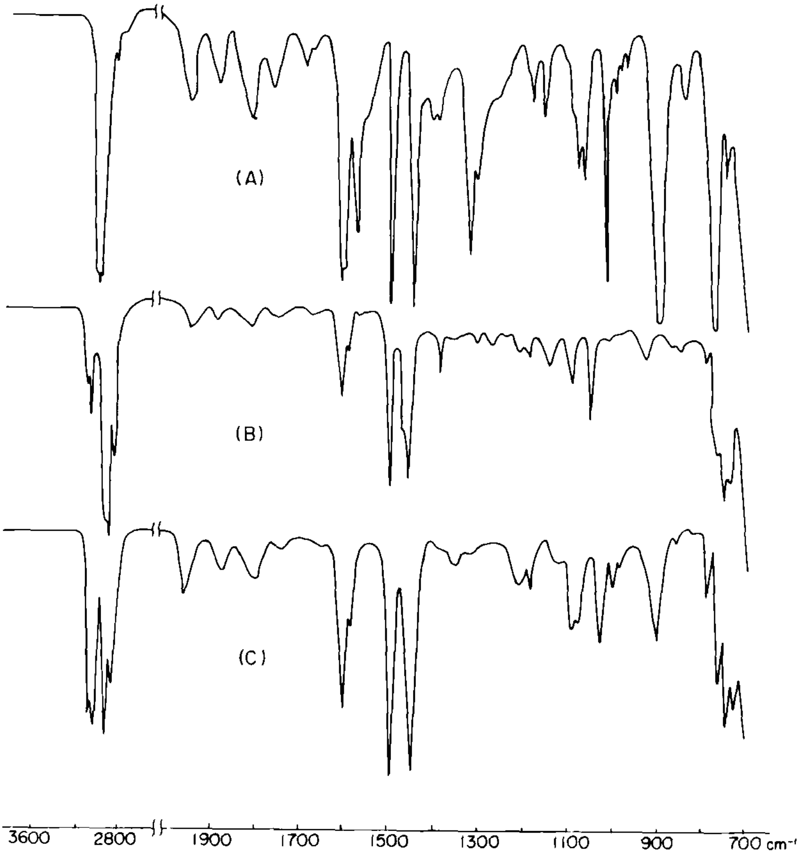

Fig. 4. Ir spectra of 1,1-diphenylethylene (A), 1,1-diphenylhexane (B), and 1,1,3-triphenylpropane (C).

lesser probability, with styrene monomer to produce the styrene anion, the styrene end group changes easily to the butadiene one because styrene anion reacts more rapidly with butadiene than with styrene monomer [2, 3]. Consequently, copolymers containing more butadiene units are formed at the initial stage of copolymerization.

With System A as catalyst, on the other hand, a large amount of styrene anion is formed at the initiation step. So far as the polymer end group of the styrene anion associated with $CH_3OCH_2CH_2OLi$ is concerned, styrene is a more reactive monomer than butadiene, though formation of butadiene end groups cannot be completely excluded. It may not be said

Table 6. NMR of DPH and TPP

τ	Assignment	Area ratio
	$CH_3(CH_2)_4CH(C_6H_5)_2$:	
7.8-9.4	$CH_3(CH_2)_4-$	11.5
6.2	$-CH(C_6H_5)_2$	1.0
2.9	C_6H_5-	10.0
	$C_6H_5CH_2CH_2CH(C_6H_5)_2$	
7.6	$-CH_2-CH_2-$	4
6.1	$-CH(C_6H_5)_2$	1
2.8	C_6H_5-	15

that butadiene (that is, allyl) anion can react with styrene in preference to butadiene monomer [16]. Butadiene anion, however, is considered to react with styrene and butadiene with a comparable rate, producing benzyl-type anion and allyl-type anion, respectively. Newly produced benzyl-type anion reacts rapidly with styrene monomer as mentioned above. Repetition of these elementary reactions can explain the rapid decrease of butadiene anion concentration in the early stages of copolymerization reaction.

Reaction Mode of System A with 1,1-Diphenylethylene

Reaction mode of System A with 1,1-diphenylethylene, which is incapable of homopolymerizing, was examined. Red precipitates were observed to form when the reaction took place. Precipitates and supernatant solution were separated, hydrolyzed, and the products were separated from one another. Identification was carried out by elemental analysis, ir, and NMR.

The reaction was considered to proceed in the following way:

$$n\text{-}C_4H_9Li + CH_2{=}C(C_6H_5)_2 \longrightarrow CH_3(CH_2)_4C(C_6H_5)_2Li$$

$$\xrightarrow{+H^+} \underset{\text{1,1-diphenylhexane (DPH)}}{CH_3(CH_2)_4CH(C_6H_5)_2} \qquad (2)$$

Table 7. Reaction of System A with 1,1-Diphenylethylene[a]

$\frac{[OLi]}{[CLi]}$	$\frac{[DPE]^b}{[CLi]}$	Reaction time (min)	Recovered DPE (mole %)	Supernatant		Precipitate	
				DPH[c] (mole %)	TPP[d] (mole %)	DPH (mole %)	TPP (mole %)
0	0.2	180	87	13	0	0	0
0.5	0.2	180	20	64	15	0	0
1.5	0.2	180	13	15	12	35	25
2.0	0.2	10	0	9	6	6	80

[a] Reaction: room temp.
[b] 1,1-Diphenylethylene.
[c] 1,1-Diphenylhexane.
[d] 1,1,3-Triphenylpropane.

$$C_6H_5CH_2Li + CH_2{=}C(C_6H_5)_2 \longrightarrow C_6H_5CH_2CH_2C(C_6H_5)_2Li$$

$$\xrightarrow{+H^+} C_6H_5CH_2CH_2CH(C_6H_5)_2$$

1,1,3-triphenylpropane (TPP)

Figures 3 and 4 show NMR and ir spectra of the products. The assignment and area ratios of NMR signals are as given in Table 6.

It is clear from the Table 6 data that the reaction mode of System A with 1,1-diphenylethylene is as written in Eqs. (2) and (3).

The results of reactions of System A with 1,1-diphenylethylene under various conditions are shown in Table 7. The relative yield of the adduct (TPP) of $C_6H_5CH_2Li$, as well as the total yield of the addition products, is found to increase with an increase in the [OLi]/[CLi] value.

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