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Reactivity of n-Butyllithium— $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ System as Catalyst for Copolymerization of Styrene with 1,3-Butadiene

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SUMMARY

Reactivity of n-butyllithium— $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ system in toluene (System N) and in cyclohexane as catalyst for copolymerization of styrene with 1,3-butadiene was studied. Copolymers obtained with System N ($[\text{OLi}]/[\text{CLi}] = 1.5$) were found to contain more styrene units than the feed monomer ratio, which also occurred with the catalyst system n-butyllithium— $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OLi}$ (System A). Pale yellow crystalline precipitates were formed in System N. The precipitates were found to have such compositions as $\text{C}_6\text{H}_5\text{CH}_2\text{Li} \cdot 2(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ and caused an enormous increase in the reactivity of styrene in the copolymerization reactions.

INTRODUCTION

It was reported in a previous paper [1] that the reactivity of the n-butyllithium($n\text{-C}_4\text{H}_9\text{Li}$)— $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OLi}$ system in toluene (System A) in styrene-butadiene copolymerization was similar to that of catalyst system $n\text{-C}_4\text{H}_9\text{Li}$ —poly(alkylene oxide) which resulted in the formation of

copolymers containing more styrene units than the feed monomer ratio at early stages of polymerization. Since the metalation reaction of toluene which produces benzyl lithium ($C_6H_5CH_2Li$) was observed to take place easily in System A, the reactivity of each of chemical species present in System A was studied [2].

This paper presents results of a study on the reactivity of the $n-C_4H_9Li-(CH_3)_2NCH_2CH_2OLi$ catalyst system in toluene (System N) and in cyclohexane in copolymerization reactions of styrene with butadiene. Copolymers obtained by System N were found to contain more styrene units than the feed monomer ratios at $[OLi]/[CLi] = 1.5$. It was anticipated that System N would show an ability to form complexes. Actually, when System N was prepared by mixing $n-C_4H_9Li$ and $(CH_3)_2NCH_2CH_2OLi$ in toluene, pale yellow crystalline precipitates were formed within several minutes (or several hours in some cases), a phenomenon which was not observed in System A. The pale yellow crystalline precipitates were found to have a composition such as $C_6H_5CH_2Li \cdot 2(CH_3)_2NCH_2CH_2OLi$, at least in the region of the feed ratio $[OLi]/[CLi] = 1.5-2.0$. The copolymerization reaction of styrene with butadiene using the crystalline precipitates as catalyst in toluene gave copolymers containing many more styrene units than those obtained by System N (feed ratio: $[OLi]/[CLi] = 1.5-2.0$).

EXPERIMENTAL

Most of the experiments were carried out under purified nitrogen atmosphere to preclude oxygen and atmospheric moisture.

Reagents

Toluene and cyclohexane were purified as usual and distilled over calcium hydride. Styrene and butadiene were purified as usual. 2-Dimethylaminoethanol was refluxed over calcium hydride and distilled; bp $134^\circ C$. $(CH_3)_2NCH_2CH_2OLi$ was prepared from 2-dimethylaminoethanol and lithium metal in cyclohexane. $n-C_4H_9Li$ was prepared from purified *n*-butyl chloride and lithium metal in purified petroleum ether [3]. Dimethyl sulfate was distilled under reduced pressure; bp $66^\circ C$ (8 mm Hg).

Procedures

The styrene-butadiene copolymerization procedures and the methods of analyzing the copolymers obtained were described in earlier publications

[1, 2]. Microstructure of butadiene units in copolymers were measured by IR spectra. Assignment of absorption bands was based on the methods of Morero et al. [4], 1,4-trans 963 cm^{-1} , 1,2- 908 cm^{-1} , and 1,4-cis 740 cm^{-1} .

The analyses of System N were carried out as follows: Samples having several $[\text{OLi}]/[\text{CLi}]$ values in feed were prepared and crystalline precipitates were allowed to separate out completely. A portion of the supernatant solution was sampled and decomposed by methanol. Regenerated 2-dimethylaminoethanol was analyzed quantitatively by vapor-phase chromatography (VPC). Another portion of the supernatant solution was sampled and treated with dimethyl sulfate. $n\text{-C}_4\text{H}_9\text{Li}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Li}$ in the supernatant solution were converted to *n*-pentane and ethylbenzene, respectively. Methylation products were analyzed quantitatively by VPC with *n*-hexane and Decaline as internal standard.

RESULTS AND DISCUSSION

1. $[\text{OLi}]/[\text{CLi}]$ Values and Reactivity of Styrene

Results of the styrene and butadiene copolymerization reaction with $n\text{-C}_4\text{H}_9\text{Li}-(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ system in toluene (System N) are shown in Table 1. System N formed crystalline precipitates and became heterogeneous; System A remained in the homogeneous state throughout the reaction.

It was found that copolymers obtained with System N ($[\text{OLi}]/[\text{CLi}] = 1.5$ in feed) possessed a little more styrene units than feed monomer ratio (3:7) when copolymerization reactions were terminated at a low conversion, while a catalyst system with $[\text{OLi}]/[\text{CLi}] = 2.0$ produced copolymers possessing nearly equal styrene units to feed ratio. Reactivity of styrene may appear somewhat higher in the catalyst system with $[\text{OLi}]/[\text{CLi}] = 1.5$ than with $[\text{OLi}]/[\text{CLi}] = 2.0$, but the slight difference in the styrene content of the copolymers should probably be ascribed to differences in conversion in the copolymerization reactions (Fig. 1).

Copolymers obtained by using the catalyst systems with $[\text{OLi}]/[\text{CLi}] < 1$ possessed fewer styrene units than feed ratio.

When the $n\text{-C}_4\text{H}_9\text{Li}-(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ catalyst system was prepared in cyclohexane, no crystalline precipitates were formed and the system remained homogeneous. Results of styrene and butadiene copolymerization with the homogeneous catalyst system are shown in Table 2. Catalyst systems with $[\text{OLi}]/[\text{CLi}] = 2.0$ and 3.0 gave copolymer containing more styrene units than feed monomer ratio (3:7), while less styrene units than

Table 1. Copolymerization of Styrene and Butadiene by System N and System A Catalysts

Additive	$\frac{[\text{OLi}]}{[\text{CLi}]}$	Polymerization time (min)	Conversion (mole %)	Styrene content (mole %)
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}^a$	0.5	118	38.3	15.0
	1.0	142	64.1	12.5
	1.5	42	11.4	32.5
		43	15.6	33.5
	2.0	41	31.5	39.5
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OLi}^b$		44	49.3	27.0
		51	59.9	29.7
		65	85.3	28.0
	1.0	30	42.1	33.9
	2.0	60	82.4	34.3
	4	53.8	50.5	

^aStyrene, 10.5 mmole; butadiene, 24.5 mmole; *n*-C₄H₉Li, 0.35 mmole; toluene, 60 ml; polymerization temp., 40°C.^bStyrene, 27 mmole; butadiene, 63 mmole; *n*-C₄H₉Li, 0.9 mmole; toluene, 15 ml; polymerization temp., 40°C.

Table 2. Copolymerization of Styrene and Butadiene by $n\text{-C}_4\text{H}_9\text{Li}-(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ System in Cyclohexane^a

Additive	$\frac{[\text{OLi}]}{[\text{CLi}]}$	Polymerization time (min)	Conversion (mole %)	Styrene content (mole %)
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$	0.5	31	31.1	13.5
	1.0	205	52.6	14.2
	1.5	97	54.9	21.0
	2.0	80	33.4	55.2
	3.0	50	38.3	43.5
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OLi}$	0.5 ^b	60	52.9	9.8
	1.0 ^b	5	40.3	33.6
	2.0	7	70.2	32.1
	3.0	5	39.6	69.6
	4.0	5	39.1	47.7

^aStyrene, 10.5 mmole; butadiene, 24.5 mmole; $n\text{-C}_4\text{H}_9\text{Li}$, 0.35 mmole; cyclohexane, 60 ml; polymerization temp., 40°C.

^bStyrene, 27 mmole; butadiene, 63 mmole; $n\text{-C}_4\text{H}_9\text{Li}$, 0.9 mmole; cyclohexane, 15 ml; polymerization temp., 40°C.

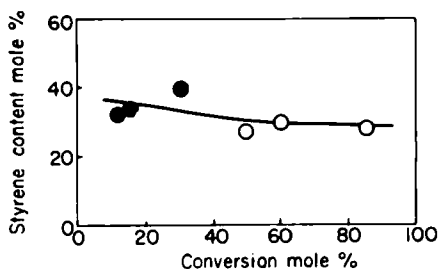


Fig. 1. Styrene-butadiene copolymerization reaction by System N.
 $[\text{OLi}]/[\text{CLi}]$ values: 1.5 (●), 2.0 (○).

feed ratio were incorporated into copolymer molecules when catalyst systems had $[\text{OLi}]/[\text{CLi}]$ values of less than 1.5 were used. The styrene content of copolymers obtained with cyclohexane as solvent increased significantly with increasing $[\text{OLi}]/[\text{CLi}]$ values from 1.5 to 2.0, which was not the case with toluene as solvent (System N).

Infrared spectra of styrene-butadiene copolymers obtained in toluene and in cyclohexane are shown in Fig. 2. The 1,2-structure of the butadiene units in copolymers is seen to increase rapidly with an increase in the ratio of $[\text{OLi}]$ to $[\text{CLi}]$, the amount of 1,4-cis structure being negligibly small in these copolymers.

2. Composition and Reactivity of System N

As mentioned above, pale yellow crystalline precipitates were separated out within several minutes (or several hours in some cases) after $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ and $n\text{-C}_4\text{H}_9\text{Li}$ were mixed in toluene. Reactivities of the supernatant solution and the crystalline precipitates in the styrene-butadiene copolymerization were examined separately. Table 3 shows the results. The copolymer obtained with the supernatant solution as catalyst contained less styrene units than feed monomer ratio (3:7) at the early stage of the copolymerization reaction. On the other hand, the crystalline precipitates which were again dissolved in toluene produced a copolymer containing much more styrene units compared to the case with System N ($[\text{OLi}]/[\text{CLi}] = 1.5\text{-}2.0$) as catalyst. These results suggest that the crystalline precipitates are composed of chemical species which play the most important role in increasing the styrene reactivity in the copolymerization.

The catalyst system was examined in detail in order to obtain information about the chemical composition of System N. The analytical method for System A, which was reported previously, was applied to System N with

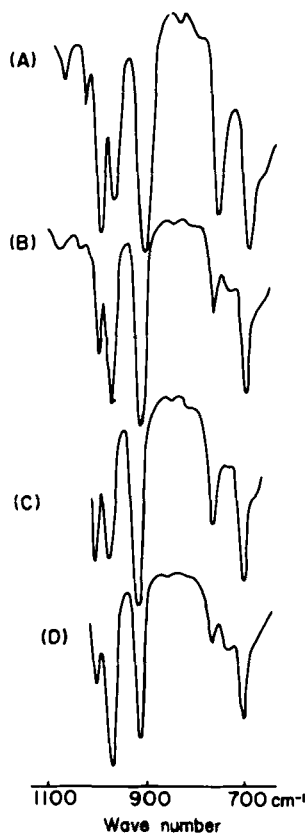


Fig. 2. IR spectra of styrene-butadiene copolymers prepared by $n\text{-C}_4\text{H}_9\text{Li}-(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ catalyst system:

	Solvent	$[\text{OLi}]/[\text{CLi}]$	Conversion (mole%)	Styrene (mole %)
(A)	Toluene	2.0	49.3	27.0
(B)	Toluene	1.0	64.1	12.5
(C)	Cyclohexane	1.5	54.9	21.0
(D)	Cyclohexane	0.5	31.1	13.5

Table 3. Copolymerization of Styrene and Butadiene with Supernatant and Precipitates of System N

Catalyst ^a	Polymerization time (min)	Conversion (mole %)	Styrene content (mole %)
Supernatant ^b	70	17.7	21.3
solution	50	26.1	19.2
Precipitates ^c	10	22.2	65.8

^a(CH₃)₂NCH₂CH₂OLi, 5.0 mmole; n-C₄H₉Li, 2.5 mmole; toluene, 10 ml.

^bStyrene, 27 mmole; butadiene, 63 mmole; toluene, 10 ml; supernatant solution, 5 ml.

^cStyrene, 15 mmole; butadiene, 35 mmole; toluene, 50 ml; precipitate, 0.2236 g.

some modifications. Narita and Tsuruta previously reported [2] that metalation reaction of toluene formed C₆H₅CH₂Li when n-C₄H₉Li and CH₃OCH₂CH₂OLi were mixed in toluene. When this system was quenched with dimethyl sulfate, n-C₄H₉Li and C₆H₅CH₂Li were converted to n-pentane and ethylbenzene, respectively, which were analyzed quantitatively by VPC. It was also shown by double titration, according to Gilman [5], that CH₃OCH₂CH₂OLi was scarcely cleaved by the organolithium reagents present in System A.

The supernatant solution and the crystalline precipitates in System N were analyzed separately. The double titration method in which a normal solution of hydrochloric acid is used was not applied to System N because of poor reproducibility due to the basic nitrogen atom of the dimethylaminoethoxide in System N. 2-Dimethylaminoethanol, recovered by adding a sample into excess methanol, was analyzed by VPC. Another sample was quenched with dimethyl sulfate, and n-pentane and ethylbenzene were analyzed by VPC.

When crystalline precipitates of System N were separated, washed thoroughly with toluene, and treated with dimethyl sulfate, ethylbenzene was detected by VPC, but no peak assignable to n-pentane being observed. It was therefore concluded that the sole organolithium compound involved in the precipitates was C₆H₅CH₂Li.*

*Metalation reaction of toluene has been reported to occur in n-C₄H₉Li-N,N,N',N'-tetramethylethylenediamine system [6-9].

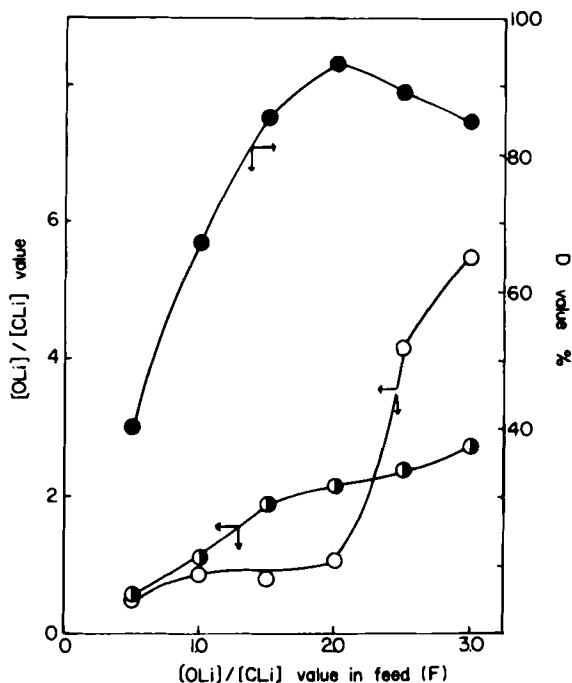


Fig. 3. Composition of $n\text{-C}_4\text{H}_9\text{Li}-(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ system in toluene. \circ : $[\text{OLi}]/[\text{CLi}]$ value in supernatant solution. \circ : $[\text{OLi}]/[\text{CLi}]$ value in the crystalline precipitates. \bullet : per cent (D) of the amount of $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ present in the crystalline precipitates to the total $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$.

Analyses of the supernatant solution of System N were carried out and the results obtained are summarized in Table 4. Some of the data in Table 4 are illustrated in Fig. 3. The ratio $[\text{OLi}]/[\text{CLi}]$ in the supernatant solution (R) scarcely increases until the ratio $[\text{OLi}]/[\text{CLi}]$ in the feed (F) reaches 2.0. A sudden increase of (R) value is seen when (F) exceeds 2.0. The per cent (D) of $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ (B) that is present in the crystalline precipitates compared to the total $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OLi}$ (A) increases rapidly until (F) attains a value of 2.0 and then decreases slowly. The composition (S) of the crystalline precipitates can be calculated from the concentration of $[\text{OLi}]$ and $[\text{CLi}]$ in the feed and in the supernatant solution. Since (S) values are actually about 2 in the region where $F = 1.5\text{-}2.0$, the crystalline precipitates produced in System N are considered to be primarily

Table 4. Composition of Supernatant Solution in System N^a

Feed		Composition of supernatant solution				Difference of concentration between feed and supernatant solution				$\frac{(B)}{(A)} \times 100$
[OLi] [CLi] (F)	[OLi] (mmole) (A)	n-C ₄ H ₉ Li (mmole)	[OLi] (mmole)	$\frac{[CLi]}{n-C_4H_9Li}$ (mmole)	$\frac{[CLi]}{C_6H_5CH_2Li}$ (mmole)	[OLi] [CLi] (R)	[OLi] (mmole) (B)	[CLi] (mmole)	[OLi] [CLi] (S)	(%) (D)
0.5	1.0	2.0	0.50	0.80	0.27	0.47	0.50	0.93	0.54	40
1.0	2.0	2.0	0.67	0.51	0.28	0.85	1.33	1.21	1.10	67
1.5	3.0	2.0	0.46	0.44	0.21	0.78	2.54	1.35	1.88	85
2.0	4.0	2.0	0.28	0.13	0.13	1.07	3.72	1.74	2.14	93
2.5	5.0	2.0	0.54	0.02	0.11	4.16	4.46	1.87	2.38	89
3.0	6.0	2.0	0.93	0.01	0.16	5.48	5.07	1.83	2.77	85

^aToluene, 17 ml; room temperature; 4 days.

composed of C₆H₅CH₂Li · 2(CH₃)₂NCH₂CH₂OLi (1:2 complex I). This conclusion is supported by two other curves in Figure 3, both of which possess inflection points at F = 2.0. At F = 1.0 and 0.5 the crystalline precipitates are presumably composed of complexes that may contain 1:1 or less (CH₃)₂NCH₂CH₂OLi.

The metalation reaction in System N is considered to proceed in such a way that some parts of *n*-C₄H₉Li aggregates are loosened by (CH₃)₂NCH₂CH₂OLi, resulting in the formation of a complex, *n*-C₄H₉Li-*n*(CH₃)₂NCH₂CH₂OLi (*n* = 1 or 2), which is able to metalate toluene to produce C₆H₅CH₂Li complexed with (CH₃)₂NCH₂CH₂OLi, the composition of which is concluded to be 1:2, at least in the region of F = 1.5 - 2.0* as discussed above.

Since a styrene-butadiene copolymer containing 65% styrene units was obtained at about 20% conversion by using the crystalline precipitates of System N (Table 3), the chemical species responsible for the enhancement of styrene reactivity was concluded to be the 1:2 complex I in the region F > 1.5. System N as a whole, however, did not increase the styrene reactivity to the extent attained by complex I as catalyst because the reactivity of complex I is screened by that of free or less complexed alkyllithium present in the supernatant solution of System N.

In the copolymerization reaction in cyclohexane, on the other hand, copolymers containing more styrene units than feed ratio are obtained when the [OLi]/[CLi] ratio is larger than 2.0. Contrary to System N, the catalyst system prepared in cyclohexane with a ratio larger than 2.0 is homogeneous and a large amount of *n*-C₄H₉Li · 2(CH₃)₂NCH₂CH₂OLi (II) is formed which is able to produce copolymers containing many styrene units. In the region where [OLi]/[CLi] < 1.0, complex II is scarcely formed and the copolymerization reaction is presumably controlled by *n*-C₄H₉Li · (CH₃)₂NCH₂CH₂OLi and/or free *n*-C₄H₉Li, which results in the formation of copolymers containing about 14% styrene units at 30-50% conversion. Intermediate results were obtained at [OLi]/[CLi] = 1.5, where the styrene content of a copolymer was about 20% at 50% conversion.

*(S) values increase gradually above F = 2.5 because of the limited solubility of (CH₃)₂NCH₂CH₂OLi.

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