

# Effects of Oxygen on Anionic Butadiene Telomerization in Hydrocarbon Solvents

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## Synopsis

During the development of an anionic butadiene telomerization process consisting of two stages, initiator preparation and telomerization, in a hydrocarbon solvent which contained a chain-transfer agent, we found that a small amount of oxygen accidentally introduced caused an unusually large decrease in the telomer viscosity. Based on the degree of such decrease due to the addition of oxygen at the two stages and based on the rather modest reactivity of oxygen with organosodium compounds, we concluded that free oxygen was catalytically involved in the telomerization process. The results of kinetic and transmetalation studies indicated that only the chain-transfer reaction was accelerated catalytically by free oxygen.

## INTRODUCTION

While we were studying a butadiene telomerization process using a benzyl sodium initiator in a hydrocarbon solvent containing such a chain-transfer agent as toluene, we noticed that contamination by even a small amount of air greatly affected the viscosities of the telomers produced. Since there was not available any quantitative investigation other than the brief one mentioned in a patent<sup>1</sup> concerning the effect of air on anionic telomerization in hydrocarbon solvents, we investigated, in particular, what component in the air and how it brought about the effects observed.

## EXPERIMENTAL

### Materials

Nippon Petrochemical Co. supplied the benzene, toluene, and butadiene. Other materials such as chlorobenzene, isopropanol, or oleic acid were of commercial reagents.

Benzene was deoxygenated by introducing dry nitrogen gas, and then dehydrated by passing it through a column packed with a silica-alumina drier (Mizusawa Chemicals' Neobead D). The oxygen and water contents (by weight) were less than 5 and 10 ppm, respectively. Toluene and chlorobenzene were deoxygenated and dehydrated by introducing dry nitrogen gas. Butadiene was dehydrated by passing it through a column packed with a silica-alumina drier (Mizusawa Chemicals' Neobead P). Isopropanol and oleic acid were used without further purification.

### Preparation of Benzyl Sodium Initiator

The following procedures were all carried out under nitrogen atmosphere. Sodium was dispersed in benzene using oleic acid as the dispersing agent at about 120° C in a pressure autoclave equipped with a high speed agitator. The benzyl sodium initiator was prepared using a modified method of Nobis and Moormeier.<sup>2</sup>

In a typical run, a sodium dispersion containing 0.22 mol of sodium metal and 0.5 mol of toluene was introduced into a 0.5 dm<sup>3</sup> autoclave. Then  $4 \times 10^{-3}$  mol of isopropanol was added followed by dropwise addition of 0.1 mol of chlorobenzene. The mixture was kept at around 30° C, and then raised to 80° C and maintained at the temperature for 2 h to complete the transmetalation reaction between phenyl sodium and toluene. The yield was 85–90%. The benzyl sodium initiator was used in a telomerization run without purification or isolation.

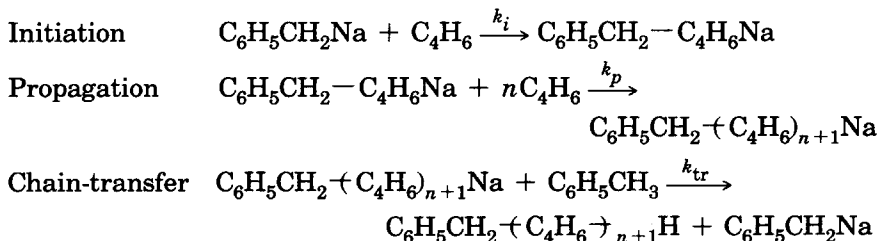
### Telomerization

Telomerization runs were all carried out in a closed system under nitrogen atmosphere.

Semicontinuous telomerization was performed as follows: 0.2 mol of the benzyl sodium initiator and 0.8 mol of toluene were charged into a 5 dm<sup>3</sup> autoclave. The total volume was adjusted to 3 dm<sup>3</sup> by adding benzene (solvent). The mixture was maintained at 30° C, and 20 mol of butadiene was added to the liquid phase in equal portions in 4.5 h. The liquid polybutadiene produced was recovered conventionally and its viscosity was measured.

Since the initiator is insoluble in the solvent and it forms a heterogeneous system, it would be difficult to make a kinetic study of such system. However, in order to get a general kinetic picture of such system, we believe it would be helpful to calculate the apparent rate constants and to evaluate their changes due to the presence of a foreign material.

We assumed that it was a living telomerization and we confirmed that one terminal end of each telomer was the benzyl group derived from benzyl sodium or toluene by a <sup>1</sup>H-NMR analysis. We applied the conventional first-order rate equation to each of the elemental reactions.



We used the most probable rate constants of initiation, propagation, and chain-transfer reactions and calculated the concentrations of the components—initiator, propagation-end, monomer, and chain-transfer agent—at a certain telomerization time by integrating the rate equations using a computer. From the results, a time vs. butadiene conversion curve and a time vs. molecular weight curve were obtained as shown in Figures 1 and

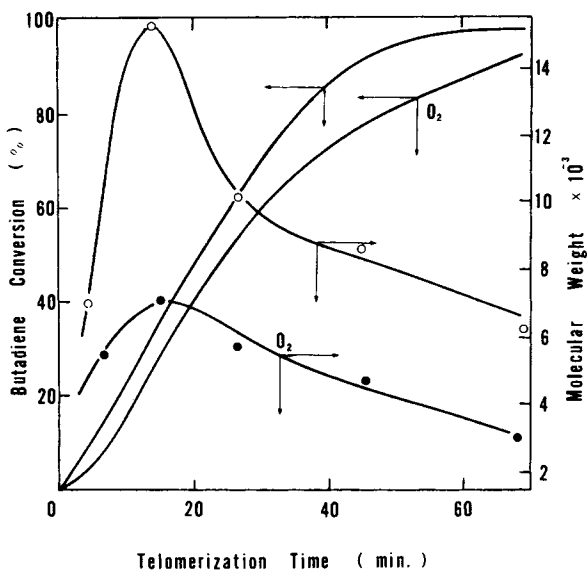


Fig. 1. Effects of oxygen on the kinetic studies of butadiene telomerization: (○)  $O_2 = 0$  mol %,  $(CH_3)_2CHONa = 0$  mol %; (●)  $O_2 = 1$  mol %,  $(CH_3)_2CHONa = 0$  mol %.

2. The most suitable apparent rate constants with a minimum deviation were determined by using a computer regression method.

In a typical procedure for kinetic studies of telomerization, 8 mol of butadiene was added all at once to a 3 dm<sup>3</sup> mixture containing 0.1 mol of the benzyl sodium initiator, 2.0 mol of toluene, and benzene (solvent) at 30° C. The pressure drop was recorded continuously, and a small amount of the mixture was withdrawn from time to time during the run to determine the number-average molecular weights of the telomers produced.

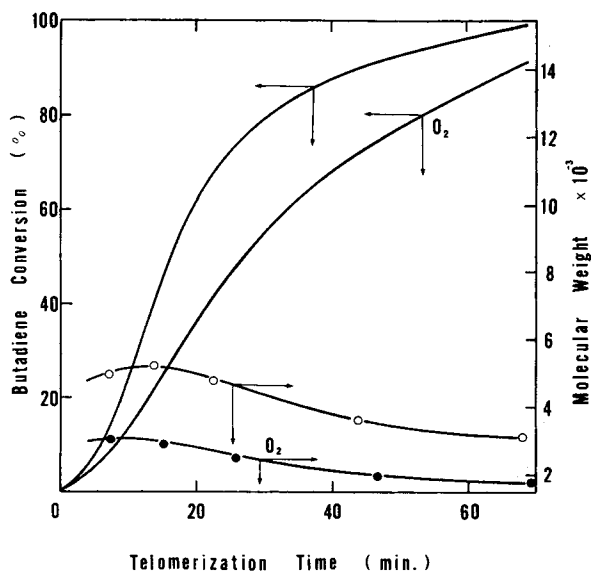


Fig. 2. Effects of oxygen on the kinetic studies of butadiene telomerization: (○)  $O_2 = 0$  mol %,  $(CH_3)_2CHONa = 4$  mol %; (●)  $O_2 = 1$  mol %,  $(CH_3)_2CHONa = 4$  mol %.

### Experimental Methods

Number-average molecular weights were determined at 37° C in benzene with a vapor pressure osmometer (Mecrolab Model 30A). Telomer viscosities were measured at 25° C using a B-type viscometer (Tokyo Keiki Model B8L). Microstructures of telomers were determined with Nihon Bunko Model DS-701G infrared spectrometer. Molecular weight distributions were determined at a room temperature on tetrahydrofuran solutions of telomers using a high-performance GPC equipped with Toyo Soda columns G-5000H6, G-4000H6, G-3000H8, and G-2000H8. The benzyl group of telomer ends was determined with a Hitachi R-24B NMR Spectrometer at 60 MHz.

### RESULTS AND DISCUSSION

To investigate which component in the air would cause the decrease in the telomer viscosity, we first added a small amount of water at the telomerization stage; however, we found it had no effect. We then introduced air or oxygen at the initiator preparation and telomerization stages. The results are shown in Figure 3 and Table I. A small amount of oxygen in the air or that dissolved in the solvent affected the viscosity significantly (in our telomerization runs, the total amount of oxygen in the reagents was assumed to be less than 0.3 mol % on the initiator). Although the viscosity decreased with increasing amount of oxygen introduced, the oxygen in the initiator preparation stage was less effective than that in the telomerization stage; especially, the oxygen added to a nontransmetalized initiator was far less effective. Microstructures of the telomers were approximately 66–68 mol % 1,2 units, 15 mol % trans 1,4 units, 15 mol % cis 1,4 units, and 2–4 mol % benzyl units. Little or no change in the microstructures of telomers was observed in these runs. Telomer molecular weight distributions ( $M_w/M_N$ ) obtained from a GPC analysis were in the range of 2–2.5. Although chromatograms shifted to a lower molecular weight region with the effect of oxygen, there was no significant change in  $M_w/M_N$ .

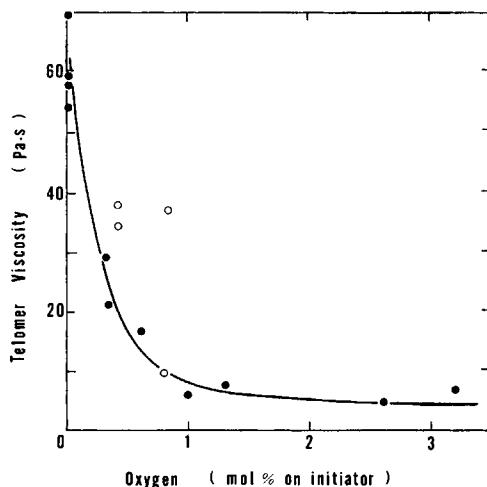


Fig. 3. Effects of oxygen on telomer viscosity in semicontinuous telomerization: (○) introduced at the initiator preparation stage; (●) introduced at the telomerization stage.

TABLE I  
Effects of Oxygen on Telomer Viscosity in Semicontinuous Telomerization

| Introduced O <sub>2</sub> (mol % on initiator) | O <sub>2</sub> source             | O <sub>2</sub> introducing stage <sup>a</sup> | Telomer viscosity (Pa s) | Butadiene conversion (%) |
|--|-----------------------------------|---|--------------------------|--------------------------|
| 0  | Control                           | —   | 53.5–69.7                | 94–100                   |
| 0.3  | Air                               | T   | 21.0                     | 99                       |
| 0.3  | O <sub>2</sub> containing benzene | T   | 29.5                     | 97                       |
| 0.4  | Air                               | I   | 38.1                     | 99                       |
| 0.4  | Air                               | Before transmetalation                        | 33.9                     | 95                       |
| 0.6  | O <sub>2</sub> containing benzene | After transmetalation                         | 16.7                     | 99                       |
| 0.8  | Air                               | I   | 37.0                     | 95                       |
| 0.8  | Air                               | Before transmetalation                        | 9.3                      | 92                       |
| 1.0  | O <sub>2</sub>                    | After transmetalation                         | 5.8                      | 81                       |
| 1.3  | Air                               | T   | 7.0                      | 84                       |
| 2.6  | Air                               | T   | 5.0                      | 52                       |
| 3.2  | Air                               | T   | 7.1                      | 42                       |

<sup>a</sup> I = introduced at the initiator preparation stage; T = introduced at the telomerization stage.

Oxygen in excess decreased the telomer yields. Since oxygen can act as a termination agent, a coupling agent or an oxidation agent, besides increasing a chain-transfer reaction, as would be described later, we assumed that the telomer yield decreasing was due to the deactivation of living telomer ends caused by oxygen in excess.

### Kinetic Studies on Oxygen Effects

Kinetic studies were made on the telomerization system in the presence of a small amount of oxygen. The results are shown in Table II and Figures 1 and 2. It was revealed that oxygen was involved only in the chain-transfer reaction. The fact that microstructures of the telomers were not affected by addition of oxygen also supports the fact that oxygen was not involved in the propagation step.

Transmetalation during the initiator preparation stage was also affected significantly by the presence of a small amount of oxygen. Table III showed that benzyl sodium yields in the initial periods of transmetalation increased remarkably with increasing amount of oxygen.

From these facts, it was concluded that oxygen affected only the chain-transfer reaction and it decreased the viscosities of the telomers produced.

### Reaction Mechanism of Oxygen

Phenyl sodium reacts with oxygen to produce peroxide which reacts successively with more phenyl sodium to form sodium phenoxide. Benzyl sodium seems to react with oxygen to produce peroxide which reacts successively with more benzyl sodium to form 1,2-diphenylethane and sodium peroxide which are similar to products formed by oxidation of diphenylmethyl sodium<sup>3,4</sup>:

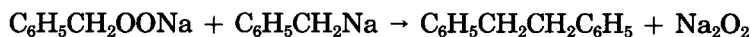
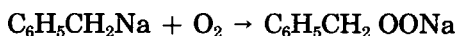
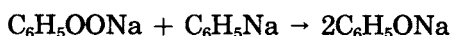
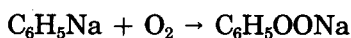


TABLE II  
Kinetic Studies

| $\text{O}_2$<br>(mol % on<br>initiator) | $(\text{CH}_3)_2\text{CHONa}$<br>(mol % on<br>initiator) | Apparent rate constants <sup>a</sup> ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) |                      |                       |
|---|--|--|----------------------|-----------------------|
|   |  | $k_i$  | $k_p$                | $k_{tr}$              |
| 0                                       | 4  | $4.5 \times 10^{-4}$   | $2.7 \times 10^{-1}$ | $5.2 \times 10^{-3}$  |
| 1                                       | 4  | $4.8 \times 10^{-4}$   | $3.1 \times 10^{-1}$ | $15.0 \times 10^{-3}$ |
| 0                                       | 0  | $1.5 \times 10^{-4}$   | $9.2 \times 10^{-1}$ | $8.2 \times 10^{-3}$  |
| 1                                       | 0  | $2.3 \times 10^{-4}$   | $6.1 \times 10^{-1}$ | $13.0 \times 10^{-3}$ |

<sup>a</sup>  $k_i$  = initiation,  $k_p$  = propagation, and  $k_{tr}$  = chain transfer.

TABLE III  
Effects of Air on Transmetalation

| Introduced air<br>(O <sub>2</sub> mol% on PhNa) | Benzyl sodium yields <sup>a</sup><br>(%) |
|---|--|
| 0.0   | 13                                       |
| 0.2   | 25                                       |
| 0.4   | 35                                       |
| 0.8   | 42                                       |

<sup>a</sup> Yields after 10 min. at 80°C.

Therefore, it is of interest to investigate whether oxygen itself or some of the reaction products of oxygen, such as peroxide derivatives or alkoxides, really affect the chain-transfer reaction.

The following three observations suggest that only free oxygen affects the chain-transfer reaction catalytically. (1) The reaction of oxygen with the organosodium compounds in the initiator was not instantaneous nor complete. We introduced 1 mol % of oxygen on benzyl sodium at the initiator preparation stage and measured the rate of oxygen consumption by gas-chromatography. After 30 min, about 15% of the oxygen remained unaffected at ambient temperature. (2) The oxygen introduced at the initiator preparation stage (I) was less effective for decreasing the telomer viscosity than that introduced at the telomerization stage (T): especially, the oxygen added to phenyl sodium (I-P) was far less effective than that added to benzyl sodium (I-B). These results are shown in Table I.

The concentration of free oxygen in telomerization seems to follow the order:



because the oxygen in the telomerization stage (T) contacts preferably with more diluted organosodium compounds than that in the initiator preparation stage (I), and the oxygen added to phenyl sodium (I-P) reacts at higher temperatures than that added to benzyl sodium (I-B). These observations support the fact that only free oxygen is effective in the chain-transfer reaction. (3) Modifications of alkali metals or organoalkali metals with alkoxides of alkali metals are well known.<sup>5-9</sup> It has been postulated that alkoxides are involved in the complexation with propagation ends and they enhance the propagation rate of butadiene polymerization. It has also been reported that the presence of an alkoxide profoundly influences the microstructure of polybutadiene. These effects on the propagation rate and microstructures occurred at the mol ratio of alkoxide to initiator of minimum 5 mol % (usually 30-50 mol %). On the other hand, the effects of oxygen were saturated when the mol ratio of oxygen to the initiator was less than 1 mol % (Fig. 3).

Although some reports about the effects of an alkoxide on the chain-transfer reaction are available,<sup>7,9</sup> no detailed work has been done. In our telomerization work, isopropanol (4 mol % on the initiator) was added at the initiator preparation stage to activate the sodium metal surface. The isopropanol seemed to have been converted to sodium isopropoxide under our reaction conditions. The effects of sodium isopropoxide are shown in Figures 1 and 2. Although both oxygen and sodium isopropoxide decreased

TABLE IV  
Effects of Organic Peroxides on Apparent Rate Constants<sup>a</sup>

| Organic peroxides   | Apparent rate constants (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ) |                      |                      |
|---|--|----------------------|----------------------|
|   | $k_i$  | $k_p$                | $k_{tr}$             |
| <i>t</i> -BuOOH   | $5.9 \times 10^{-4}$   | $1.2 \times 10^{-1}$ | $2.3 \times 10^{-3}$ |
| C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> OOH  | $5.9 \times 10^{-4}$   | $1.2 \times 10^{-1}$ | $2.2 \times 10^{-3}$ |
| <i>t</i> -BuOO <i>t</i> -Bu   | $5.1 \times 10^{-4}$   | $2.3 \times 10^{-1}$ | $4.4 \times 10^{-3}$ |
| C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> | $3.6 \times 10^{-4}$   | $2.3 \times 10^{-1}$ | $2.3 \times 10^{-3}$ |

<sup>a</sup> Organic peroxide, 1.0 mol % on initiator.

the molecular weights of the telomers, we believe that the mechanism of each modifier for such decrease would be different. From the kinetic studies, we were aware that oxygen was involved only in the chain-transfer reaction; on the other hand, sodium isopropoxide was involved in increasing the initiation rate by affecting the aggregation conditions of the initiator.

Kinetic studies were made by introducing at the telomerization stage a small amount of each of the various organic peroxides. Although these organic peroxides are expected to react with organosodium compounds to give correspondent organoalkali peroxides or alkoxides, they had but no effect on increasing the chain-transfer reaction as shown in Table IV. Moreover, a small amount of *t*-butylhydroperoxide did not affect the telomer viscosity in semicontinuous telomerization at all.

The above observations, (1), (2), and (3), suggest that free oxygen affects the chain-transfer reaction catalytically.

The true mechanism of the oxygen effect on the butadiene telomerization, up to now, is still unknown. Much additional work is needed to elucidate the mechanism.

## CONCLUSION

From the result of butadiene telomerization using a benzyl sodium initiator in a hydrocarbon solvent which contained a chain-transfer agent (toluene), we observed that free oxygen present in the two stages decreased the viscosities of the telomers formed catalytically and significantly. It was confirmed from the results of kinetic and transmetalation studies that oxygen accelerated only the chain-transfer reaction which decreased the telomer viscosity. Since the decrease in the molecular weight depends on at which stage oxygen is introduced, and since the reactivity of oxygen towards organosodium compounds is rather modest, we conclude that free oxygen is involved catalytically only in the chain-transfer reaction.

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