

Studies on Chain Transfer Reaction in Butadiene Polymerization Initiated with *n*-Butyl Lithium and Novel Promoter Potassium *para*-Methylphenoxide

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ABSTRACT: The chain transfer reaction was examined in the anionic telomerization of butadiene with *n*-BuLi as the initiator, potassium *para*-methylphenoxide (ROK) as the novel promoter, mixed xylene as the transfer agent as well as a solvent in the presence of diglyme as the polar modifier. Effects of ROK, diglyme, and the polymerizing temperature were studied. It was demonstrated that they all promote the

chain transfer reaction. The relative constant of chain transfer to the solvent was also calculated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1215–1218, 2005

Key words: anionic polymerization; polybutadiene; chain transfer; polymerization kinetics; molecular weight distribution

INTRODUCTION

Potassium *tert*-butoxide (*t*-BuOK) is a typical promoter in use today for the industrial production of liquid rubber. Studies on the polymerization kinetics and chain transfer reaction of dienes with *t*-BuOK involved in the initiator system have been widely reported.^{1–9} However, because *t*-BuOK is synthesized through a fierce reaction of *tert*-butanol and the highly inflammable metal potassium, it is neither safe nor economical to prepare, especially when in suit. Moreover, the solubility of *t*-BuOK in hydrocarbon solvents is limited, which influences the exact preparation and transportation of the promoter and thus the realization of the designed molecular weight and microstructure of the produced polymer.

Phenoxides, however, can be prepared by reacting phenols with KOH, which is much cheaper than potassium, because of the stronger acidities of phenols and the much milder reaction. Their solubilities are improved by the contribution of the aromatic structure. Their effects as polymerizing promoters have also been proved.^{10–12} All of these may lead to a better choice of promoter in the anionic polymerization of dienes and styrene.

In this communication, the chain transfer reaction in the anionic telomerization of butadiene with *n*-butyl lithium (*n*-BuLi) as the initiator, potassium *para*-meth-

ylphenoxide (ROK) as the promoter, xylene as the transfer agent as well as the solvent in the presence of diglyme as the polar modifier was examined for the first time on the basis of a kinetic study on the same system.¹⁰

EXPERIMENTAL

Materials

The materials were prepared and refined as described in our earlier publication.¹⁰ ROK was prepared by heating to reflux a stirred mixture of KOH and ROH in a stoichiometric ratio with xylene as the solvent. The azeotroped water was collected in a Dean Stark trap. When the theoretical amount of water was removed, the mixture that was produced was washed 3–5 times with refined cyclohexane and then evacuated.

ROK was dissolved in tetrahydrofuran (THF, 10 mass % ROK) before being mixed with a measured amount of *n*-BuLi in refined cyclohexane to form the complex initiator. Note that, although THF is a common modifier in anionic polymerization, its effect on the polymerization kinetics and chain transfer reaction is much weaker within the experimental range (THF/Li = 5.5–18.2) compared with diglyme and ROK. Thus, the discussion of the present study does not focus on it.

Polymerization procedure

A solution of 10 mass % butadiene in mixed xylene (49.9% *m*-, 22.9% *p*-, 12.5% *o*-, 14.7% ethylbenzene)

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TABLE I
Number-Average Molecular Weight (M_n), Chain Transfer Number (N_t), and polydispersity (PD) of PB at Different K/Li Ratios at 50°C

K/Li		0	0.3	0.5	0.8	1
G/Li = 0	M_n	70041	4181	3742	2301	2098
	N_t	0.02	16.07	18.08	30.03	33.03
	PD	1.03	2.42	2.26	3.62	3.26
G/Li = 1.0	M_n	61808	2644	2440	1857	1486
	N_t	0.2	26.0	28.3	37.4	47.1
	PD	1.12	3.66	3.7	3.77	4.15

Complete monomer conversion was decided for each experiment.

with a certain amount of diglyme was charged into polymerizing bottles under nitrogen pressure and brought to the desired reaction temperature (T) by tumbling the bottles in a constant temperature bath. Small amounts of impurities present in the polymerization systems were scavenged by the addition of n -BuLi before the stoichiometric amount of complex initiator (1.4 mmol n -BuLi/100 g butadiene, i.e., $[\text{BuLi}]_0 = 1.17 \text{ mmol L}^{-1}$ unless otherwise indicated) was introduced. The final point of scavenging was indicated by the appearance of a greenish-yellow color caused by the presence of diglyme, and the scavenger level varied from 0.2 to 0.4 mmol/L. At the desired time, isopropanol was added to terminate the reaction together with an antioxidant, 2,6-di-*tert*-butyl-4-methylphenol dissolved in toluene, the mass of which was 1% of that of dry rubber. Each sample was then dried in a vacuum oven to obtain conversion so that its relationship to the polymerizing time was determined.

Characterization

The number-average molecular weights (M_n) and molecular weight distributions (i.e., polydispersities, PD)

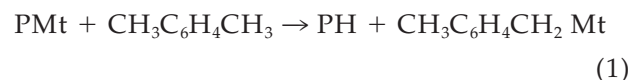
of the polymer products were measured by GPC (PL-GPC220, Polymer Laboratories).

RESULTS AND DISCUSSION

Kinetic scheme of telomerization

The telomerization mechanism of butadiene with toluene as the telogen has been illustrated in detail by Luxton.¹¹ Xylene has been proved to be an active chain transfer agent as capable as toluene⁷ but with lower toxicity and the mechanism is similar, as described below.

Transmetalation takes place in the presence of xylene in addition to the normal initiation and propagation reactions.



The $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Mt}$ product can further initiate propagation and transmetalation. This recycle mecha-

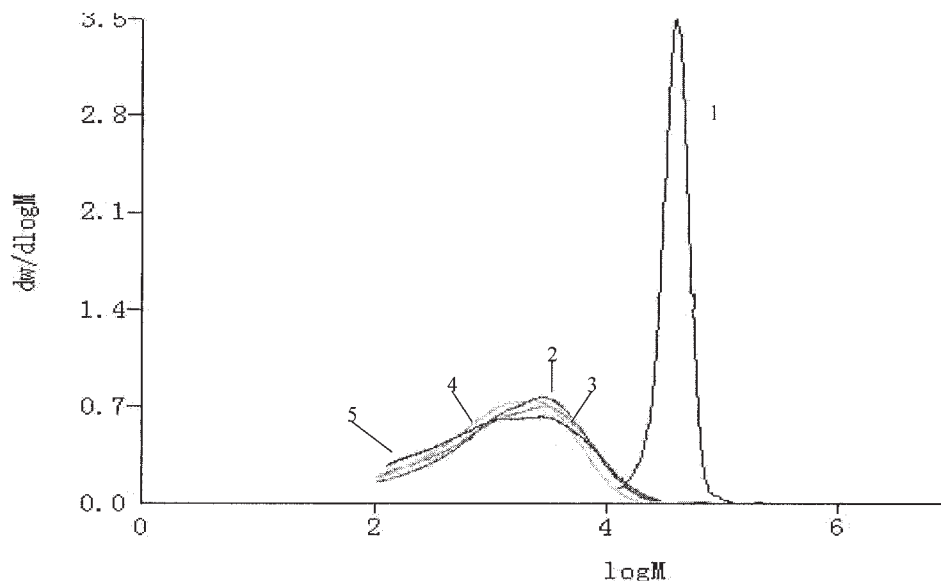


Figure 1 A plot of $dw/d \log M$ versus $\log M$ of PB with G/Li = 1.0 and $T = 50^\circ\text{C}$. 1: K/Li = 0; 2: K/Li = 0.3; 3: K/Li = 0.5; 4: K/Li = 0.8; 5: K/Li = 1.0

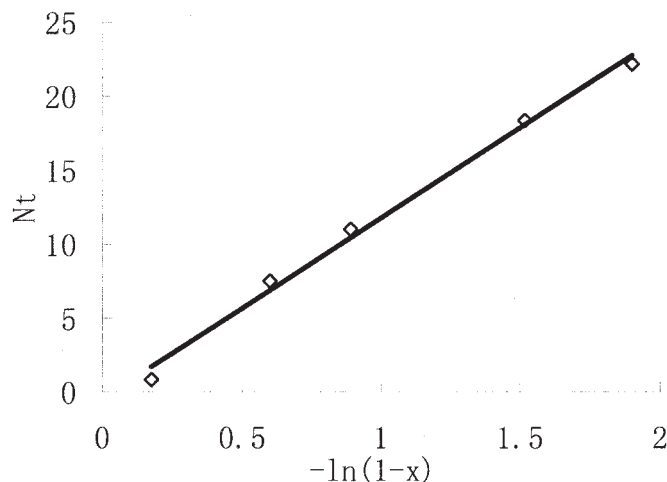
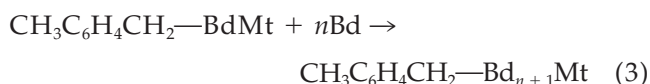
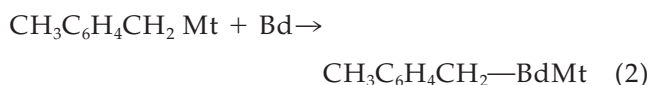


Figure 2 The polymerization of butadiene: N_t versus $-\ln(1-x)$, $G/Li = 1.0$, $K/Li = 1.0$, and $T = 45^\circ\text{C}$.

nism results in polymers with lower molecular weights and broader PDs than originally designed.



Note that the mechanism of the process is rather complicated and includes many other reactions like metal–metal exchange, association–dissociation, and so forth, which are not discussed in this work.

Effect of K/Li on M_n and PD

The chain transfer number (N_t) was defined as follows:

$$N_t = M_{\text{th}} / M_n - 1 \quad (4)$$

where the theoretically expected molecular weight (M_{th}) is

$$M_{\text{th}} = [M]_0 \cdot x / [I]_0 \quad (5)$$

and x , $[M]_0$, and $[I]_0$ are the conversion, the initial monomer concentration, and initial initiator concentration, respectively. The values of the M_n , N_t , and PD of polybutadienes (PBs) prepared at different K/Li mole ratios were obtained and are provided in Table I.

As the K/Li ratio was raised, the M_n of the PB product decreased, the N_t increased, and the corresponding PD was broadened. Figure 1 demonstrates this trend well with the K/Li of each curve increasing in turn from the right to the left. This suggested that

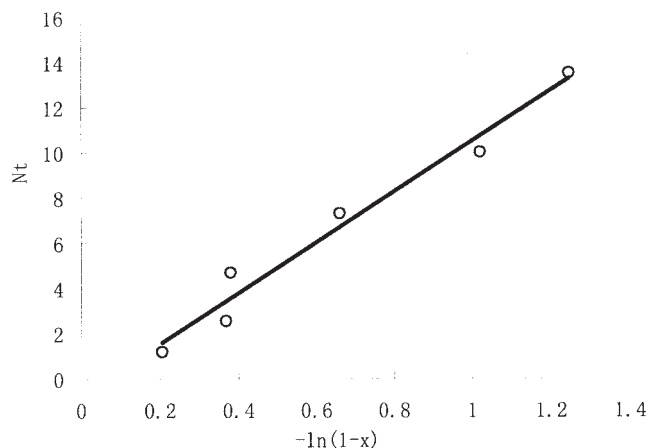


Figure 3 The polymerization of butadiene: N_t versus $-\ln(1-x)$, $G/Li = 1.0$, $K/Li = 1.0$, and $T = 50^\circ\text{C}$.

the presence of ROK prompted the chain transfer reaction so that the M_n dropped to 1500 from the designed value (71,400) and the N_t rose to 47 as the K/Li ratio increased from 0 to 1.0 when $G/Li = 1.0$.

A study of the $K/Li = 1.0$ and $G/Li = 1.0$ system was then made in particular as the chain transfer tendency therein was so obvious.

Quantitative study of chain transfer reaction

The relative constant of the chain transfer to the solvent (C_{tr}) was calculated according to the expression of Gatzke¹³:

$$N_t = -C_{\text{tr}}[RH]_0 \ln(1-x) / [I]_0 \quad (6)$$

where N_t is the chain transfer number as defined above and $[RH]_0$ and $[I]_0$ are the initial chain transfer

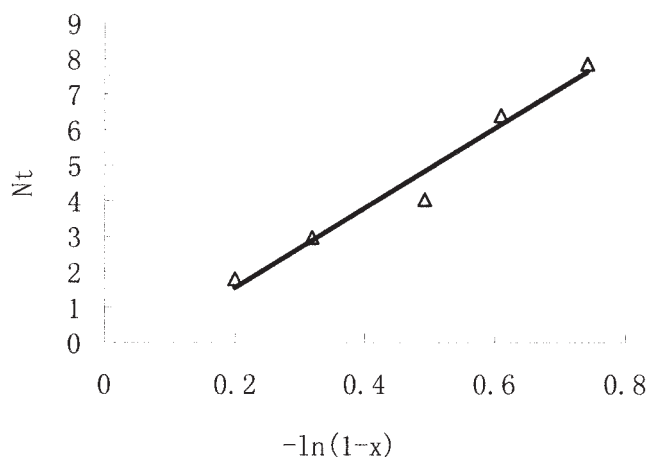


Figure 4 The polymerization of butadiene: N_t versus $-\ln(1-x)$, $G/Li = 1.0$, $K/Li = 1.0$, and $T = 60^\circ\text{C}$.

TABLE II
Relative Constant of Chain Transfer (C_{tr}) of 1,3-Butadiene (G/Li = 1.0 and K/Li = 1.0)

T (°C)	45	50	60
$C_{tr} \times 10^3$	1.94	2.00	2.20

agent and effective initiator concentration, respectively.

By plotting the line on N_t versus $-\ln(1-x)$, we got the C_{tr} value from the slope (Figs. 2–4 and Table II).

Effect of temperature on chain transfer reaction

Table II shows that the C_{tr} increased as the polymerizing temperature was raised.

The M_n , N_t , and PD values of the polymers obtained at different temperatures are listed in Table III. It was apparent that, for the same telomerization system, the M_n dropped as the temperature was raised whereas the N_t and PD both rose, which illustrated the chain transfer reaction rate was accelerated more by the temperature rising than the propagation rate. It can be deduced that the activation energy of the chain transfer reaction is greater than that of propagation (32.07 kJ/mol),¹⁰ that is, the former reaction is more sensitive to temperature than the latter.

Effect of ROK on chain transfer reaction of butadiene

When an organolithium initiator is used in a telomerization process, the presence of a polar promoter is necessary to obtain adequate rates of transmetalation at convenient temperatures and metal alkoxides and tetramethylethylenediamine (TMEDA) are typical promoters.¹¹ Although diglyme is a strong kind of modifier comparable to TMEDA, its effect on the chain

TABLE III
Effect of Temperature on the Number-Average Molecular Weight (M_n), Chain Transfer Number (N_t), and Polydispersity (PD) of PB

T (°C)	40	50	60
M_n	1662	1540	1481
N_t	42.0	45.4	47.2
PD	3.76	4.11	3.90

TABLE IV
Effects of Diglyme and ROK on the Chain Transfer in Butadiene Polymerization at 50°C

	M_n	N_t	PD	$C_{tr} \times 10^3$
G/Li = 0, K/Li = 0	70,041	0.02	1.03	0.01
G/Li = 1.0 K/Li = 0	61,808	0.2	1.12	0.03
G/Li = 1.0 K/Li = 1.0	1,486	47.1	4.15	2.00

transfer reaction does not seem to be obvious. Table IV suggests that the N_t of systems with the mere addition of diglyme remains lower than 1. This is because diglyme can only affect the polarity of C—Li bonds and the degree of tightness of ion pairs in the system through its influence on disassociation of and complexation with the Li species. However, these effects do not seem to be crucial to the chain transfer reaction. In contrast, the addition of ROK creates C—K bonds in the system and their activities in metalation are somewhat greater than C—Li bonds, so the contribution of ROK is more significant than diglyme when added on the same scale.

CONCLUSION

The chain transfer reaction in the *n*-BuLi/ROK/diglyme/xylene/butadiene system was studied and the M_n and PD of the polymers that were produced were measured. It was concluded that ROK prompts the chain transfer reaction in this system by the formation of C—K bonds. The rise of the polymerization temperature also favors the chain transfer process.

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