Polymerization Kinetics of Liquid Polybutadiene Using Potassium Para-Methylphenoxide as Promoter*

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Abstract: In this communication, polymerization kinetics of the anionic telomerization of butadiene with *n*-BuLi as the initiator, potassium para-methylphenoxide (ROK) as the promoter, xylene as the transfer agent as well as the solvent in the presence of diglycoldimethylether (2G) as the polar modifier was studied. Effects of $n(K)/n(Li)$, $n(2G)/n(Li)$ and temperature on polymerization were investigated. It is determined that polymerization rate is first-order in monomer concentration. Raising $n(K)/n(Li)$, $n(2G)/n(Li)$ and temperature all resulted in increasing of the false first-order apparent rate constant of propagation. Influence of different reaction conditions on the molecular weight and microstructure of the produced polymer is examined. Liquid polybutadiene produced this way can be used as material for green coating.

Key words: green coating; liquid polybutadiene; kinetics; polymerization rate; microstucture
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Most kinds of fine polymeric coatings in use today containing noxious volatile solvent (VOC), which has been the second serious pollution source to the city environment after auto emission, it has become the focus of attention to develop water – soluble green coating. Research on liquid polybutadiene used as material for green coating has been reported home and abroad[1-3] as well as kinetics of the polymeric system using *n*-BuLi as the initiator and potassium *t*-butoxide (*t*-BuOK) as the promoter[4-6], but not has the polymerization kinetics of the anionic telomerization of butadiene with *n*-BuLi as the initiator, ROK as the promoter, xylene as the transfer agent as well as the solvent in the presence of 2G as the polar modifier. In this communication, ROK was used instead of *t*-BuOK aiming at a securer producing process, a more feasible transportation and a preciser preparation of the promoter in the industrial production of liquid polybutadiene, which might diversify the anionic polymerization promoters. By studying the polymerization kinetics and structure of the polymer, kinetic parameters under different conditions were obtained and the telomerization effect of ROK was tested, which may offer reference and basis to the innovation of initiator system in the liquid polybutadiene production.

1 Experiments

1.1 Materials

N_2, butadiene, 2G and solvent were refined, *n*-BuLi was produced and analyzed, and the polymerizing solution was prepared in the manner previously described[3]. ROK was prepared by reacting KOH with para-methylphenol in xylene. After being washed for several times with the solvent and dried in vacuum, the produced ROK was transferred and kept in a sealed container. And the whole process was under refined N_2.

1.2 Experiment and testing

The complex initiator was prepared by solving ROK in THF before the addition of measured amount of *n*-BuLi. Polymerization procedure was described before[3]. Polymerization velocity of butadiene was measured by use of dilatometer. All reactions were carried out at 40 ℃ and the monomer and initiator concentration were $w = 10\%$ and 1.16 mmol/L, respectively, unless otherwise indicated.

Inherent viscosity of polymer was measured by use of Ubbelohde viscosimeter. Number-average molecular weight ($\overline{M_n}$) was tested by KNAUER Model Ⅱ vapor-pressure osmometer. And the polymer microstructure was obtained with Nicolet Model 20DXB infrared spectrometer.

2 Results and discussion

Kinetic behavior of butadiene polymerization at different $n(K)/n(Li)$, $n(2G)/n(Li)$ ratios and temperatures was observed.

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2.1 Effect of $n(K)/n(Li)$ on k_p''

Relationship between x and t when $n(2G)/n(Li) = 0$ and $n(K)/n(Li) = 0 \sim 1.0$ at 40 ℃ was illustrated in Fig. 1. It seems that when $n(K)/n(Li)$ is raised, there is an augment of C – K bonds in the system, which results in the increase of polymerization rate of butadiene.

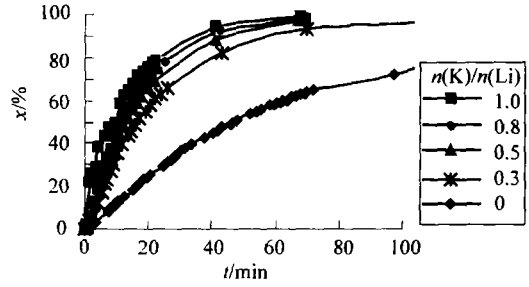

Fig. 1 Plot of x vs. t when $n(2G)/n(Li) = 0$ at 40 ℃

According to the expression

$$-\frac{d[M]}{dt} = k_p[C]^{\alpha}[M]^{\beta} \quad (1)$$

if reaction rate is assumed to be first-order in monomer concentration, e.g. $\beta = 1$ and let $k_p'' = k_p[C]^{\alpha}$,

$$-\frac{d[M]}{dt} = k_p''[M] \quad (2)$$

By rewriting (2) and then integrating it, one obtains

$$-\ln(1-x) = k_p''t \quad (3)$$

Fig. 2 is drawn on $-\ln(1-x)$ vs. t which reveals a well linear relationship between them and the false first-order apparent rate constants of propagation (k_p'') at different $n(K)/n(Li)$ ratios were obtained from the slope of the lines. It can be seen that when $n(K)/n(Li)$ is raised, k_p'' increases, which is also applicable when $n(2G)/n(Li) = 1.0$.

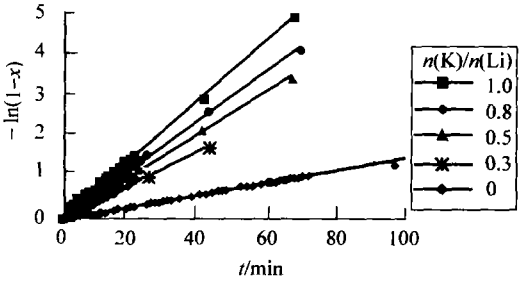

Fig. 2 Plot of $-\ln(1-x)$ vs. t when $n(2G)/n(Li) = 0$ at 40 ℃

2.2 Effect of $n(2G)/n(Li)$ on k_p''

Fig. 3 shows that the addition of 2G enhances k_p'' when $n(K)/n(Li)$ is in the range of $0 \sim 1.0$ and the upward trend is more obvious at higher $n(K)/n(Li)$ ratios, which suggests a diversification of active centers and a shift of the equilibrium among these centers in the system caused by the addition of polar modifier and the new created centers seem to prompt the telomeric effect of ROK.

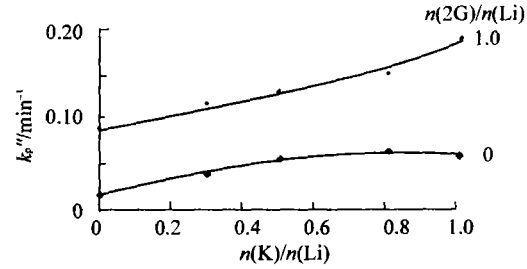

Fig. 3 Effect of $n(K)/n(Li)$ on k_p'' at 40 ℃

2.3 Effect of polymerization temperature(θ) on k_p''

Polymerization was carried out at 40, 50, 60 ℃ respectively and the corresponding values of k_p'' are listed in Tab. 1. It is apparent that the raise of θ favors the reaction. k_p'' approximately doubles per 10 ℃ increase for systems without 2G while for those with 2G the effect of θ is comparatively less.

Tab. 1 Effect of θ on k_p''/min^{-1}

	θ/℃		
	40	50	60
$\frac{n(2G)}{n(Li)} = 0, \frac{n(K)}{n(Li)} = 0$	0.0156	0.0450	0.0947
$\frac{n(2G)}{n(Li)} = 1.0, \frac{n(K)}{n(Li)} = 0$	0.0874	0.1125	0.1258
$\frac{n(2G)}{n(Li)} = 0, \frac{n(K)}{n(Li)} = 1.0$	0.0670	0.1666	0.2832

2.4 Microstructure of polybutadiene

The analytical results of polymer characterization are summarized in Fig. 4. In the experimental range vinyl content of polybutadiene increases from 14.4% to ca. 51% when $n(2G)/n(Li) = 0$ and decreases from 75.7% to ca. 52% when $n(2G)/n(Li) = 1.0$ as $n(K)/n(Li)$ goes up. But the changing tendency is not so considerable when $n(K)/n(Li) > 0.5$.

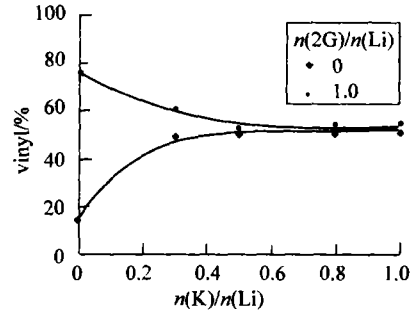

Fig. 4 Microstructure of polybutadiene when $\theta = 40$ ℃

It is supposed to be PLi (single and aggregated) and the complex of PLi·ROK etc. in the system as the active centers and the C – K bonds thereof are believed to

prompt the formation of 1,2- structure. In addition, Zhou et al[5,6] suggested the existence of PK·PLi·ROLi when $0 < n(K)/n(Li) < 0.5$ in the *t*-BuOK/*n*-BuLi/TMEDA/toluene system they studied and considered its contribution to 1,2- structure equivalent to PLi·ROK while when $n(K)/n(Li) > 0.5$, PLi·ROK became the main reactive species again and the change of $n(K)/n(Li)$ ratio didn't affect the polymer microstructure much. In this research work, the changing trend of vinyl content with the increase of $n(K)/n(Li)$ is very alike to that of theirs and thus similar reactive species are supposed to be created. When 2G is added, it forms further complex with PLi, PLi·ROK and PK·PLi·ROLi among which PLi·2G is believed to contribute most to the 1,2- structure, which results in a decrease of vinyl content as $n(K)/n(Li)$ rises in the presence of 2G.

2.5 Molecular weight of polybutadiene

Fig. 5 demonstrates the relationship of $\overline{M_n}$ versus $n(K)/n(Li)$ and $n(2G)/n(Li)$. In the range of 0 ~ 1.0, $\overline{M_n}$ decreases as $n(K)/n(Li)$ is raised and doesn't change much when $n(K)/n(Li) > 0.5$, which is more evident in the presence of 2G. It seems the C – K bonds in the complexes are highly active and can enhance the chain transfer reactions to both the monomer and xylene.

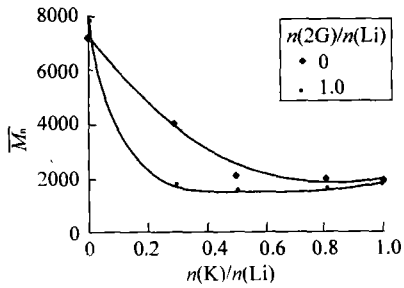

Fig.5 $\overline{M_n}$ of polybutadiene when $\theta = 40℃$

3 Conclusion

(1) Polymerization rate is first-order in monomer concentration in the range of $n(K)/n(Li) = 0 \sim 1.0$ at 40 ℃. k_p'' increases as $n(K)/n(Li)$ rises and the addition of 2G also enhances it.

(2) Rate of polymerization is dependent on temperature and for systems without 2G k_p'' approximately doubles per 10 ℃ temperature increase.

(3) In the experimental range, vinyl content of polybutadiene increases from 14.4% to ca.51% when $n(2G)/n(Li) = 0$ and decreases from 75.7% to ca.52% when $n(2G)/n(Li) = 1.0$ as $n(K)/n(Li)$ goes up.

(4) $\overline{M_n}$ decreases from the designed value to below 2000 as $n(K)/n(Li)$ rises in the experimental range and the addition of 2G enhances the tendency.

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酚钾盐为助引发剂的液体聚丁二烯调聚动力学

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摘 要: 对以正丁基锂为引发剂、对甲基苯酚钾为助引发剂、二甲苯为溶剂兼作链转移剂、2G 为极性调节剂的丁二烯阴离子调聚动力学进行了研究。考察了不同 $n(K)/n(Li)$、$n(2G)/n(Li)$和温度对聚合的影响。结果表明,反应速率与单体浓度呈一次方关系,$n(K)/n(Li)$、$n(2G)/n(Li)$增大、温度升高,聚合反应表观增长速率增大,考察了不同条件对聚合物分子量及微观结构的影响。制得的液体聚丁二烯调聚物可用作绿色涂料的原料。

关键词: 绿色涂料;液体聚丁二烯;动力学;聚合速率;微观结构
中图分类号: TQ33 **文献标识码:** A