Anionic Telomerization of Diene with Potassium Dimethylphenoxide as Promoter*

REN Yan[1], *WANG Yu rong*[1], *LIU Hai feng*[1], *LIN Chun qing*[2], *ZHANG Chun qing*[1]
(1. College of Chemical Engineering, Dalian University of Technology, Dalian 116012, China;
2. Dalian Power Supply Company, Dalian 116011, China)

Abstract: In this communication, anionic telomerization of butadiene and isoprene with *n*-BuLi as the initiator, potassium dimethylphenoxide (D-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. Solubility of D-ROK in tetrahydrofuran (THF) at different temperature was investigated. Effects of D-ROK / *n*-BuLi on intrinsic viscosity ([η]), chain transfer number (Nt), relative molecular mass ($\overline{M_n}$) and microstructure of the polymers were examined. Raising D-ROK / *n*-BuLi resulted in increasing of N_t and deceasing of [η] and Mn. Liquid rubber produced this way can be used as material for green coating.

Key words: green coating; liquid rubber; chain transfer number; relative molecular mass; microstructure
CLC number: TQ317 **Document code**: A **Article ID**: 0529-6579 (2005) S2-0036-03

At present, quite a lot of fine polymeric coatings in use contain noxious volatile solvent (VOC), which do a lot harm to human beings and environment. Water-soluble coating, a kind of green coating, has the advantages of economy, environmental protection and safety, and it has become the focus of attention. Studies on liquid rubber initiated with potassium *tert*-butoxide (*t*-BuOK) used as material for green coating have been widely reported[1—4]. However, as *t*-BuOK is synthesized through fierce reaction of tert-butanol and the highly inflammable metal K, it is neither safe nor economical to prepare. What's more, the solubility of *t*-BuOK in hydrocarbon solvents is limited. In this communication, D-ROK was used instead of *t*-BuOK aiming at a securer producing process and good solubility. The anionic telomerization of diene with *n*-BuLi as the initiator, potassium D-ROK as the promoter, xylene as the transfer agent as well as the solvent in the presence of 2G as the polar modifier was studied. Solubility of D-ROK in THF at different temperature was also investigated. By studying the physical properties of polymers, the telomerization effect of D-ROK was distinct, which may offer a better choice of initiator system in liquid rubber production.

1 Experiments

1.1 Materials

D-ROK was prepared by reacting potassium hydroxide (KOH) with dimethylphenol in xylene. After being washed for several times with the solvent and dried in vacuum, the produced D-ROK was transferred and kept in a sealed container. The whole process was under refined N_2. Other materials were prepared and refined as described in our earlier publication[3].

1.2 Experiment and testing

D-ROK was dissolved in THF before mixed with measure amount of *n*-BuLi in cyclohexane to form the complex initiator. Polymerization procedure was described before[3]. All reactions were carried out at 50 ℃, 2G / *n*-BuLi (molar ratio) was 1.0, and the monomer and initiator concentration were 10% (wt) and 1.16 mmol/L, respectively, unless otherwise indicated.

Relative molecular mass ($\overline{M_n}$) and relative molecular mass distribution (PD) of produced polymers were measured by GPC (PL-GPC220, Polymer Laboratories, British). Intrinsic viscosity ([η]) was measured by use of Ubbelohde viscosimeter, and the microstructure was obtained with Nicolet Model 20DXB infrared spectrometer.

2 Results and discussion

2.1 Solubility

The solubility of different kinds of potassium phenoxides at 15, 40, 50, 60 ℃ in THF was observed as shown in Table 1. It can be seen that the solubility of D-ROK is once higher than that of potassium methylphenoxide, and with the raise of soluble temperature the solubility increas-

* 收稿日期: 2005—07—10
作者简介: 任艳 (1980 年生), 女, 研究生; 通讯联系人: 王玉荣, E-mail: lab2004@163.com

es remarkably. This was mainly because that there was an additional electron pushing methyl in dimethylphenol, which increased the electron cloud density on the benzene ring through the cooperation of conjugative effect and inductive effect. As a result, the acidity of dimethylphenol was debased and the solubility was increased.

Tab. 1　Solubility of different kinds of potassiumphenoxides in THF

Temperature (T/℃)	Solubility in THF (wt%)		
	o-ROK	*m*-ROK	*D*-ROK
15	17	15	43
40	18	20	55
50	18	20	60
60	18	20	70

2.2　Effect of D-ROK / *n*-BuLi on polyisoprene (PI)

When 2G / *n*-BuLi was 1.0, polymerization temperature was 50 ℃ and polymerization time was 1.5 h, the anionic telomerization with different amount of D-ROK / *n*-BuLi was examined.

Chain transfer number (Nt) is an important parameter in chain transfer reaction. The definition of Nt is as followed:

$$N_t = \overline{M_n(T)} / \overline{M_n} - 1$$

where $\overline{M_n(T)}$ can be described as $\overline{M_n(T)} = M_0 \cdot x / C_0$; where x is conversion, M_0 is initial concentration of monomer, and C_0 is initial concentration of initiator.

Tab. 2 shows the influence of D-ROK / *n*-BuLi on x%, $[\eta]$, $\overline{M_n}$. And *Nt* of PI. According to Tab. 2, when D-ROK / *n*-BuLi increased from 0.1 ~ 2.0, the reaction entirely completed, and $[\eta]$ of the produced polymer decreased from 47.82 to 4.86 correspondingly, especially when D-ROK / *n*-BuLi = 1.2, $\overline{M_n}$ dropped to the bottom at 893 while N_t raised to the top at 79.

Tab 2　Influence of D-ROK/*n*-BuLi on x%, $[\eta]$, $\overline{M_n}$, and N_t of PI

D-ROK / *n*-BuLi (molar ratio)	X%	$[\eta]$ /(ml·g^{-1})	$\overline{M_n}$	N_t
0.1	98.3	47.82	29250	2
0.3	95.8	25.23	8503	7
0.5	93.9	6.5	1458	48
0.8	103.5	5.47	1125	62
1.2	104.3	4.86	893	79
1.5	106.8	5.56	1186	59
2.0	102.5	5.91	1256	56

When D-ROK / *n*-BuLi was in the range of 0 ~ 1.0, the effect on PD was illustrated in Table 3. Adding promoter to the system, PD broadened and as D-ROK / *n*-BuLi increased, PD straightly raised from 1.13 to 2.52. In the case of adding D-ROK, the C—K bonds were formed, which greatly improved the activity of chain transfer reaction, therefore, N_t increased, $\overline{M_n}$ decreased and PD broadened.

Tab 3　Effect of D-ROK / *n*-BuLi on PD of PI

D-ROK / *n*-BuLi (molar ratio)	0	0.1	0.3	0.8	1.0
$\overline{M_w}/\overline{M_n}$	1.13	1.15	1.75	2.49	2.52

2.3　Effect of D-ROK / *n*-BuLi on polybutadiene (PB)

The polymerization system was the same as PI except the monomer butadiene.

Tab. 4 shows the influence of D-ROK / *n*-BuLi on PB. According to Tab. 4, with D-ROK as promter, $[\eta]$ and $\overline{M_n}$ of the polymer fell sharply. When D-ROK / *n*-BuLi was greater than 0.8, the change varied little and N_t became greater than 60. It indicated that the category and amount of the active species in the polymerization system increased because of D-ROK. As a result of the chain transfer reaction, $\overline{M_n}$ dropped more than 60 times as compared to the stoichiometric molecular mass.

Tab. 4 Influence of D-ROK/*n*-BuLi on $[\eta]$, $\overline{M_n}$ and N_t of PB

D-ROK/*n*-BuLi (molar ratio)	$[\eta]$ /(ml·g^{-1})	$\overline{M_n}$	N_t
0.1	53.23	34530	1
0.5	25.09	2401	29
0.8	11.54	1144	64
1.0	12.58	1324	55
1.5	10.48	1066	69
2.0	10.93	1102	66

It was reported that polymerization rate of isoprene was slower than that of butadiene[5-6]. This was mainly because there was a methyl in isoprene structure which formed a conjugative system with double bond. Therefore chain propagation rate of PI decreased while chain transfer dominanted the reaction, and of PI was lower than that of PB.

2.4　Effect of D-ROK / *n*-BuLi on microstructure

Fig. 1 and Fig. 2 demonstrate the effects of D-ROK / *n*-BuLi on microstructure of PI and PB respectively. Fig. 1 shows that when D-ROK / *n*-BuLi increased, 1, 4-unit increased while 1, 2-unit + 3, 4-unit gradually dropped, and in Fig. 2 it has the same trend.

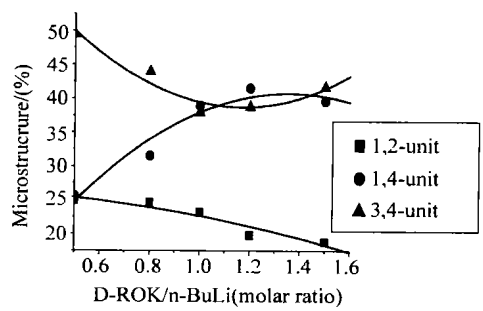

Fig 1　Effect of D-ROK / *n*-BuLi on microstructure of PI

This indicates that when adding D-ROK, a new active centre was formed, which adjusted the category and amount of the old active specied. As a result, the insert mode had a different effect and contribution to the polymers.

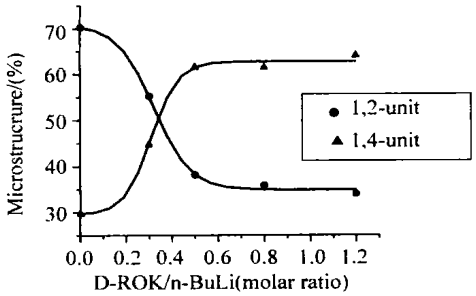

Fig 2 Effect of D-ROK / *n*-BuLi on microstructure of PB

3 Conclusions

(1) The solubility of D-ROK is once higher than that of potassium methylphenoxide, and with the raise of soluble temperature the solubility increases remarkably.

(2) With the rising of D-ROK / *n*-BuLi, $x\%$ and N_t of PI increase while $[\eta]$ and M_n decrease. PB has the same trend.

(3) Telomerization of D-ROK on PI is more notable than that of PB.

(4) When D-ROK / *n*-BuLi increases, 1, 4-unit of PI increases, 1, 2-unit + 3, 4-unit gradually dropped; and PB has the same trend.

References:

[1] WANG W, WANG Q. Liquid Polybutadiene and its application to paint [J]. Chemistry and adhesion, 1994, 4: 223—228.

[2] HSIEH H L, WOFFORD C F. Alkyllithium and alkali metal tert—butoxide as polymerization initiator [J]. J Polym Sci: Part A—1, 1969, 7 (2): 449—460

[3] SUN S S, PAN Z Y, GU M C. Synthesis of Liquid Polybutadiene (I) The Effect of Various Alkalimetal Alkoxides on Synthesis of Liquid Polybutadiene [J]. China Synthetic Rubber Industry, 1987, 10 (4): 253—257.

[4] ZHOU G B, XU G J, LI J J. A study of butadiene/toluene/potassium butoxide—n—butyllithium polymerization system. III Chain transfer [J]. China Applied Chem, 1988, 5 (2): 23—28.

[5] YE M. Dalian University of Technology [Masteral Dissertation].

[6] ZHAO B Z. Dalian University of Technology [Masteral Dissertation].

二甲基苯酚钾作助引发剂的烯烃阴离子调节聚合

任 艳[1]，王玉荣[1]，刘海峰[1]，林春清[2]，张春庆[1]

（1. 大连理工大学 化工学院，辽宁 大连 116012；
2. 大连供电公司，辽宁 大连 116011）

摘 要：采用合成时环境友好，在四氢呋喃中溶解性良好的二甲基苯酚钾作助引发剂，正丁基锂为引发剂、二甲苯为溶剂兼作链转移剂、2G 为极性调节剂对二烯烃阴离子调聚进行了研究。考察了不同 D-ROK / n-BuLi 对聚合物的特性粘度、分子量、分子量分布及微观结构的影响关系。制得的液体聚丁二烯和聚异戊二烯可用作绿色涂料的原料。

关键词：绿色涂料；液体橡胶；链转移次数；相对分子量；微观结构

中图分类号：TQ317