

Fe-Al 络合催化苯乙烯-马来酸酐交替共聚^{*}

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摘 要 应用 $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ (acac = 乙酰丙酮) 催化苯乙烯-马来酸酐共聚, 制得富于交替的白色粉末共聚物. 共聚反应动力学研究表明, 共聚反应与单体浓度呈一级关系, 表观活化能为 48.6 kJ/mol.

关键词 铁络合催化剂, 苯乙烯, 马来酸酐

本文在铁系催化聚合丁二烯^[1]的研究基础上, 将这一类催化剂应用于苯乙烯和马来酸酐交替共聚, 这是继 Bartlett^[2]和杨慕杰等^[3]报道自由基方法和稀土催化苯乙烯-马来酸酐共聚以来的又一新方法, 也是铁络合催化聚合研究的又一新进展. 本文研究了铁络合催化苯乙烯和马来酸酐交替共聚规律和动力学, 用元素分析法测定了共聚物的组成. 研究表明, $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 催化剂催化苯乙烯和马来酸酐共聚可在短时间内制得交替共聚物.

1 实验部分

1.1 原料及试剂

苯乙烯(S 或 St) 上海试剂一厂出品经减压蒸馏精制, 马来酸酐(MA) 为上海化学试剂总厂出品, 用氯仿重结晶纯化, 真空干燥. 苯、甲苯、四氢呋喃、石油醚等为分析纯试剂, 用前经分子筛浸泡, 三异丁基铝系 ROTH 产品, 高纯氮系市售品. 乙酰丙酮铁用 FeCl_3 溶液和乙酰丙酮络合产生, 用四氢呋喃重结晶制得.

1.2 聚合与聚合物分析

聚合操作在氮气氛中进行, 采用真空抽烤充氮处理的单口聚合瓶, 在瓶中加入马来酸酐、溶剂、苯乙烯和催化剂, 在恒温下聚合数小时后, 加入含 5% 盐酸的乙醇溶液终止反应, 共聚物用苯抽提纯化.

共聚物的红外光谱用 PARAGON-1000 光谱仪测得. 粘度 $[\eta]$ 是以丙酮为溶剂, 在 30℃ 测定, 按一点法计算; 共聚物的分子量 ($\bar{M}_n$) 按文献[4]公式计算, $[\eta] = 8.69 \times 10^{-5} M_n^{0.74}$ (dL/g), 元素分析采用 Carlo-Erba1106 型元素分析仪测定, 共聚物组成是采用元素分析定量共聚物中的氧含量进行计算.

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2 结果与讨论

2.1 苯乙烯与马来酸酐共聚物的结构和性质

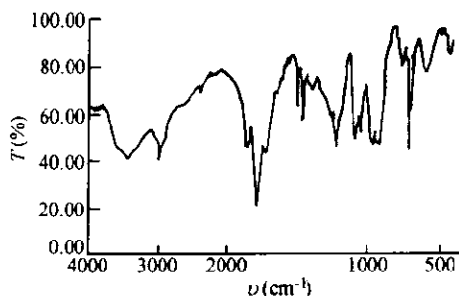


Fig.1 Infrared spectrum of maleic anhydride and styrene copolymer

$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 催化苯乙烯与马来酸酐共聚得到白色固体,可溶于丙酮,不溶于氯仿,乙醇,苯等溶剂,图 1 是苯乙烯与马来酸酐共聚物(SMA)的红外光谱,从谱图可见,除显示共聚物中苯乙烯单元的特征吸收 704cm^{-1} 和 763cm^{-1} 外,而在 1777cm^{-1} 处出现 SMA 共聚物的特征吸收^[3].

$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 催化剂在苯溶液中 50°C 下不能使苯乙烯、马来酸酐两单体均聚,但能使苯乙烯和马来酸酐共聚.表 1 是不同单体比所得共聚物,据元素定量分析计算得

到的苯乙烯和马来酸酐含量,从表 1 可见,在马来酸酐与苯乙烯摩尔比为 0.5~2 范围内,都可以得到交替共聚物.

Table 1 Influence of monomer ratio on maleic anhydride (MA) and styrene (St) copolymer composition

$[\text{MA}]/[\text{St}]$ (molar ratio)	Yield (%)	$\bar{M}_n$	Copolymer f_{MA}	Composition (%) f_{St}
2	38.3	1.12×10^5	54.6	45.4
1	68.3	1.94×10^5	53.3	46.7
0.5	35.0	1.53×10^5	52.2	47.8

Al/Fe (molar ratio) = 4; total monomer concentration = 4mol/L ; 50°C ; 3h; solvent; benzene; $[\text{Fe}] = 2.0 \times 10^{-2}\text{mol/L}$

2.2 共聚合反应特征

$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 催化苯乙烯和马来酸酐共聚合反应可以在多种溶剂中进行(表 2),但共聚物收率和分子量在苯、甲苯中较其它溶剂中高,其中石油醚中的分子量为最大.

在配位催化体系中添加第三组份,数据见表 3,加料顺序为 $\text{MA} \rightarrow \text{Sol.} \rightarrow \text{St} \rightarrow$ 第三组份 $\rightarrow \text{Cat.}$ 从表中可见,只有加入 CCl_4 时共聚物收率有明显提高,其它都有不同程度的降低,其中吡啶降低最为明显.分子量都有不同程度的下降.

Table 2 Influence of solvent on maleic anhydride and styrene copolymerization

Solvent	Yield (%)	$\bar{M}_n$
Benzene	68.3	1.94×10^5
Toluene	65.8	1.79×10^5
THF	10.1	0.24×10^5
Cyclohexane	15.4	1.19×10^5
Petroleum ether	6.3	3.45×10^5
Anisole	18.5	1.25×10^5

Monomer molar ratio 1:1, the others are same as in

Table 3 Influence of third composition on the copolymerization

Third composition	Yield (%)	$\bar{M}_n$
α, α' -Dipyridy	56.3	0.91×10^5
8-hydroxy quindine	50.7	1.25×10^5
Pyridine	16.6	0.29×10^5
Tetrachloro-methane	81.3	1.22×10^5
Acetone	60.5	0.87×10^5
No third composition	68.3	1.94×10^5

Monomer molar ratio 1:1, third composition is 0.1% monomer weight, solvent; benzene, the others are same as in Table 1

Al/Fe 摩尔比、催化剂浓度、聚合时间、聚合温度、单体总浓度等的改变对聚合反应的影响列于表 4. 数据表明,随 Al/Fe 摩尔比的增大,收率减少,分子量增大. 随着催化剂浓度的增大收率增大,而分子量随催化剂浓度增大而变小. 较好浓度为 $[Fe] = 1.5 \sim 2.0 \times 10^{-2} \text{mol/L}$. 反应温度升高收率增大,分子量变小,较好的温度为 $50 \sim 60^{\circ}\text{C}$. 单体总浓度升高收率和分子量均增大,较好的浓度为 4mol . 收率和分子量随反应时间的增长而增加.

Table 4 Influences of reaction conditions on the copolymerization

Reaction temperature ($^{\circ}\text{C}$)	Reaction time (h)	Al/Fe (molar ratio)	Catalyst concentration [Fe](mol/L)	Total monomer concentration (mol/L)	Yield (%)	$\overline{M}_n$ ($\times 10^{-5}$)
50	3	2	2.0×10^{-2}	4	69.3	1.70
50	3	4	2.0×10^{-2}	4	68.3	1.94
50	3	6	2.0×10^{-2}	4	64.8	2.10
50	3	8	2.0×10^{-2}	4	63.9	2.32
50	3	10	2.0×10^{-2}	4	63.4	2.41
50	3	12	2.0×10^{-2}	4	62.4	2.68
50	3	14	2.0×10^{-2}	4	61.2	2.69
50	3	4	2.5×10^{-2}	4	71.2	1.86
50	3	4	2.0×10^{-2}	4	68.3	1.94
50	3	4	1.5×10^{-2}	4	51.6	2.00
50	3	4	1.0×10^{-2}	4	28.3	2.12
50	3	4	0.5×10^{-2}	4	21.9	2.33
RT	3	4	2.0×10^{-2}	4	35.2	2.44
40	3	4	2.0×10^{-2}	4	49.1	2.18
50	3	4	2.0×10^{-2}	4	68.3	1.94
60	3	4	2.0×10^{-2}	4	69.3	1.79
70	3	4	2.0×10^{-2}	4	75.3	1.60
50	3	4	2.0×10^{-2}	0.5	2.5	0.37
50	3	4	2.0×10^{-2}	1	10.6	0.53
50	3	4	2.0×10^{-2}	2	24.8	1.16
50	3	4	2.0×10^{-2}	3	48.6	1.35
50	3	4	2.0×10^{-2}	4	68.3	1.94
50	1	4	2.0×10^{-2}	4	33.5	1.61
50	2	4	2.0×10^{-2}	4	49.1	1.80
50	3	4	2.0×10^{-2}	4	68.3	1.94
50	4	4	2.0×10^{-2}	4	72.4	2.16
50	5	4	2.0×10^{-2}	4	79.6	2.31

Solvent: benzene; monomer ratio; 1:1; RT: room temperature

3 共聚合反应动力学

图 2 为 $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 催化剂催化苯乙烯与马来酸酐共聚合的反应时间(t)对收率(C)作图, $\ln 1/(1-C)$ 与 t 呈线性关系, 表明共聚反应对单体浓度呈一级关系。

图 3 是催化剂浓度对聚合速度的影响, 当 $[\text{Fe}] \leq 2.1 \times 10^{-2} \text{ mol/L}$ 时反应速度呈线性增加, 当继续增大时, 则反应速度下降。

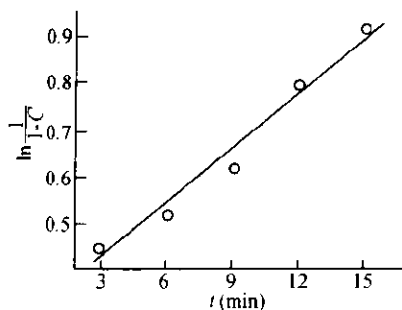


Fig. 2 Dependence of copolymer yield on the reaction time

Monomer molar ratio = 1 : 1; $T = 60^\circ\text{C}$; the others are same as in Table 1

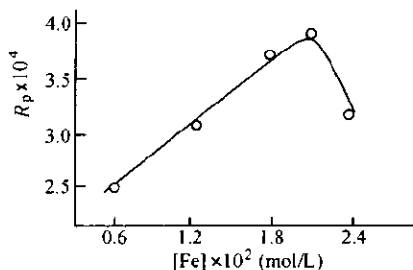


Fig. 3 Dependence of copolymerization rate on the catalyst concentration

Monomer molar ratio = 1 : 1, the others are same as in Table 1

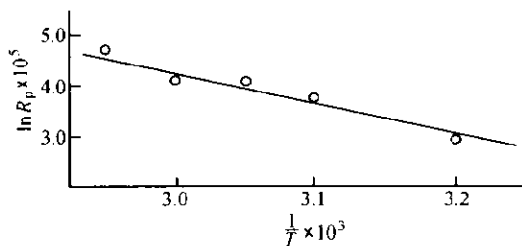


Fig. 4 Dependence of copolymerization rate on the reaction temperature

不同反应温度下的反应速率常数 K_p 对 $1/T$ 作图, $\ln K_p$ 与 $1/T$ 呈线性关系, 依据直线斜率, 用阿仑尼乌斯公式求得共聚合反应表观活化能为 48.6 kJ/mol (图 4)。

$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 络合催化苯乙烯与马来酸酐共聚, 具有低的聚合反应活化能 48.6 kJ/mol , 显示配位聚合的特征外, 对苯二酚在聚合体系中不起阻聚作用 (表 5), 也显示了配位型共聚的特征。

Table 5 Influences of paradihydroxybenzene on the copolymerization

Catalyst	Yield(%)
$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$	68.3
$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3 + \text{paradihydroxybenzene}$	67.5

The paradihydroxybenzene is 0.1% monomer weight; monomer ratio 1 : 1; the others are same as in Table 1

综上所述, 铁络合催化剂能使苯乙烯-马来酸酐进行自己共聚, 制得富于交替共聚物。

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ALTERNATING COPOLYMERIZATION OF STYRENE AND MALEIC ANHYDRIDE WITH Fe-Al COMPLEX CATALYST

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Abstract The characteristics and product structure of alternating copolymerization of styrene with maleic anhydride catalyzed by $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ are presented and discussed in the present paper. The copolymer was characterized by IR and elementary analysis. The copolymer is a product of high alternation. Maleic anhydride and styrene are 53.3% and 46.7%, respectively in the copolymer. The copolymerization can be realized in the solvents such as aromatic hydrocarbon and alkane. The yield is higher in aromatic hydrocarbon than in the others. The third composition exerts a great influence on the copolymerization. Molecular weight and yield of copolymer are lower with the third composition of α, α' -dipyridel, 8-hydroxy quindine, pyridine and acetone than that without the third composition. The yield of copolymer is higher with the third composition of tetrachoro-methane than that without the third composition. Molecular weight of copolymer increases as Al/Fe molar ratio increases. But the yield of copolymer decreases as Al/Fe molar ratio increases. The suitable Al/Fe molar ratio is four. The yield of copolymer increases and molecular weight decreases as concentration of catalysts increases. The suitable concentration of catalysts is $[\text{Fe}] = 1.5 \times 10^{-2} \text{ mol/L}$. The copolymerization can be obtained at room temperature, however, the increasing reaction temperature causes an increase of the copolymer yield and a drop of molecular weight of the polymer produced. The suitable temperature is $50 \sim 60^\circ\text{C}$. The yield and molecular weight of the polymer grow with increasing polymerization time. The kinetic studies indicate that the rate of copolymerization reaction is first order with respect to monomer concentration. E equals 48.6 kJ/mol. The reaction mechanism studies indicate that the copolymerization reaction exhibits the coordinate mechanism.

Key words Fe-Al complex catalyst, Alternating copolymerization, Maleic anhydride, Styrene