

双金属催化环氧化物聚合动力学研究*

吴立传 余爱芳 张 敏 陈立班**

(中国科学院广州化学研究所 广州 510650)

摘 要 研究了双金属氰化物络合催化剂 DMC 催化环氧丙烷聚合的动力学.用测定反应过程体系压力变化来决定聚合的起始速率,发现聚合反应速率正比于催化剂用量 C ,单体浓度 M 的平方.该实验规律可以从单体参与链引发的动力学特点解释.考察了温度对聚合反应速率的影响并求得了表观活化能为 $59.1 \text{ kJ} \cdot \text{mol}^{-1}$,该值与环氧聚合的卟啉铝、稀土络合物等催化体系接近.

关键词 双金属催化剂,环氧丙烷,环氧化物,开环聚合,动力学

环氧化物开环聚合的机理和动力学已经有过报道^[1,2].对于许多催化体系,包括路易斯酸、稀土和卟啉铝等,反应速率对单体浓度和催化剂用量均呈一级关系.双金属氰化物络合催化剂-六氰合钴酸锌络合物催化剂(DMC)用于环氧化物聚合是近年聚醚合成的重要方向之一^[3,4].DMC 属于配位催化剂,活性极高,由其合成的聚醚产品质量优异,有广阔的应用前景.该体系反应往往需要较高温度和一定的压力,研究其动力学有一定的困难.杨淑英等^[5]曾报道过类似的双金属催化剂 PBM 用于二氧化碳与环氧丙烷(PO)调节共聚合,发现其聚合动力学与普通催化剂不同,并解释了反应速率与环氧单体浓度的 2 次方成正比的实验事实.本文对 DMC 催化环氧丙烷均聚反应的研究表明,这种双金属催化剂也有类似的动力学特征.

1 实验部分

1.1 原料

甲苯,分析纯;环氧丙烷,工业级;均用 3Å 分子筛多次干燥,水分含量在 150×10^{-6} (质量分数)以下.双金属氰化物络合催化剂(DMC)按文献[6]自制.

1.2 水分测定

各种原料中的水分按照国家标准 GB12008.6-89,用卡尔·费休(Karl Fischer)法在 KF-1 型水分测定仪上测定.

1.3 诱导期和起始反应速率的确定

在干燥的带压力表的 0.1 L 高压釜内,加入适量的 DMC 催化剂,抽真空,充氮气.将釜放置恒温油浴中,经充分预热至设定温度(除特别说明外均为 105°C)后,用压力针筒迅速注入计量的甲苯和 PO,开动电磁搅拌,记录釜内压力随时间的变化,绘制压力-时间关系图(图 1).曲线上的 A 点为加料时刻. AB 段和 BC 段对应于所加物料的升温过程.反应起动后体系压力下降.因反应物浓度不断降低,降压速率逐渐变小(图中 C 点至 D 点).根据体系传热等因素不同,BC 段的压力急升的情况有时也可能不出现.统一定义到达 C 点的时间 t_0 为诱导期.用计算机画出 CD 段的拟合曲线及其在 C 点处的切线,该切线 CE 的斜率的绝对值 ρ (即 $-\text{d}p/\text{d}t$) 代表反应的起始(最大)速率.

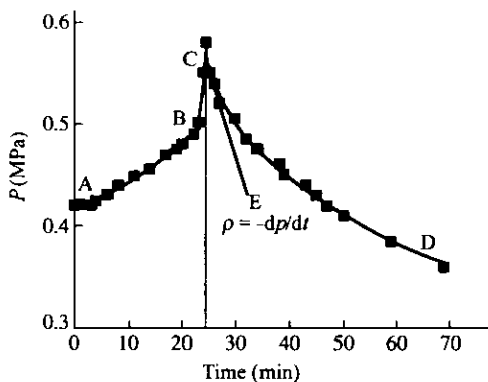


Fig. 1 Observed pressure during PO polymerization catalyzed by DMC

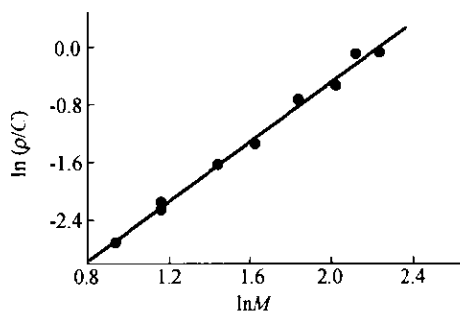


Fig. 3 Initiative reaction rate depending on monomer concentration

Slope = 2.08, regression coefficient = 0.998; Relative deviation = 2.6%; C : $\text{g} \cdot \text{L}^{-1}$; ρ (i. e., $-\text{dp}/\text{dt}$): $\text{MPa} \cdot \text{min}^{-1}$; M : $\text{mol} \cdot \text{L}^{-1}$; DMC content: 0.05 wt% based on PO

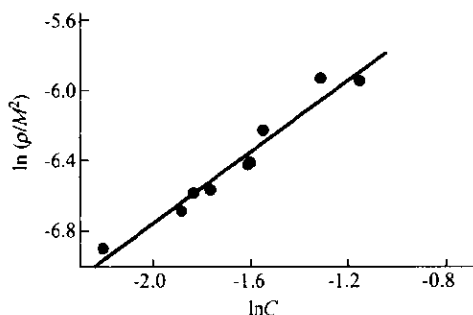


Fig. 4 Initiative reaction rate depending on catalyst concentration

Slope = 1.01, regression coefficient = 0.977; Relative deviation = 8.3%

2.3 温度对聚合反应速率的影响

在 70 ~ 115℃ 范围内和在甲苯溶液中,不加调节剂,用 DMC 催化 PO 聚合,测定了反应初始降压速率 ρ . 将 ρ 除以 $M^2 C$ 后取对数,对温度倒数作图得到较好的直线关系(图 5). 根据 Arrhenius 公式从直线斜率算出 DMC 催化 PO 聚合反应的表现活化能为 $59.1 \text{ kJ} \cdot \text{mol}^{-1}$. 此数值与实验中采用的催化剂批号有关,与卟啉金属的 $50.4 \text{ kJ} \cdot \text{mol}^{-1}$ ^[2] 和稀土催化体系的 $61.3 \text{ kJ} \cdot \text{mol}^{-1}$ ^[1] 接近,这表明 DMC 是一类优良的催化剂.

2.4 动力学方程的推导

已经阐明双金属催化剂用于环氧化物与二氧化碳共聚时,链引发必须有环氧单体参加方能实现^[5]. DMC 聚醚合成可以看成上述反应在二氧化碳浓度为零时的一个特例,故也有相似的特征. 即

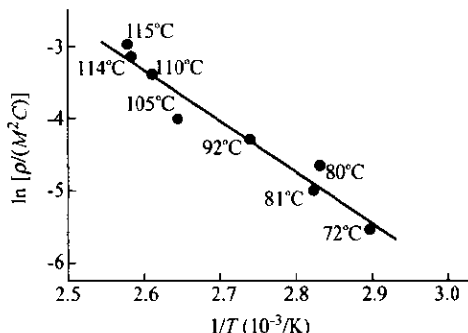
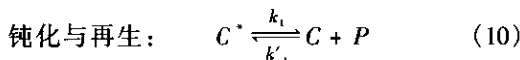
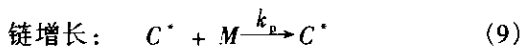
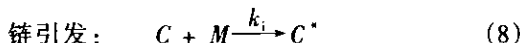


Fig. 5 Effect of temperature on polymerization rate of PO

PO 9 mL; Toluene 9 mL; DMC 0.05 wt% based on PO;

Regression coefficient = 0.977; Relative deviation = 8.2%

DMC 催化剂不可能自行活化,它必须与环氧单体的相互作用中才能形成活性中心而完成链引发反应. 因此动力学的基元反应可用下面方程式(8)~(10)表示;其中 C^* 是单位体积中活性中心的摩尔数.



假设恒稳状态下活性中心 C^* 的浓度不变:

$$\frac{\text{d}C^*}{\text{d}t} = k_i CM + k'_i CP - k_t C^* = 0$$

$$\text{得 } C^* = (k_i M + k'_i P) C / k_t \quad (11)$$

$$\text{因为 } R_p = -\text{d}M/\text{d}t = k_p C^* M$$

以式(11)代入,如果 $k_i M > k'_i P$, 解得聚合速率为:

$$R_p = k_p k_i M^2 C / k_t$$

记 $K = k_p k_i / k_t$, 则

$$R_p = K M^2 C \quad (12)$$

式(12)就是推导的动力学方程. 它从反应历程说明了实验得到的结果.

动力学研究的过程中还涉及了反应诱导期的问题. 发现诱导期与温度、浓度等许多因素有关. 此外,双金属氰化物络合物催化环氧丙烷聚合时常要加入含活泼氢的化合物来调节产物的分子量. 调节剂的加入量对聚合速率有很大的影响. 动力学研究中对调节聚合的反应机理也有新的揭示. 所有这些将另文讨论.

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KINETICS OF DOUBLE METAL CYANIDE COMPLEX CATALYZED
PROPYLENE OXIDE POLYMERIZATION

WU Lichuan, YU Aifang, ZHANG Min, CHEN Liban

(Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650)

Abstract The kinetics of polymerization of propylene oxide (PO) catalyzed by zinc hexacyanocobaltate complex catalyst was studied by means of pressure measurements. All the reactions were carried out in 0.1 L autoclaves equipped with manometers. As soon as the pressure of the system began to decrease, the polymerization was considered to have been initiated. By evaluation of vapor - liquid equilibrium of toluene solutions of propylene oxide, the pressure was found to linearly depend on the PO volume fraction. Therefore, the rate of the reaction was known to be proportional to the rate of pressure decreasing. The influence of reaction temperature, catalyst and monomer concentrations on the reaction rate was investigated. It was found that the polymerization was a first order reaction to the concentration of catalyst C , but a second order reaction to that of monomer M as shown in the following equation. The rates also depended on reaction temperature while the apparent activation energy was 59.1 kJ/mol according to the Arrhenius equation. It was proposed that the epoxide monomer must be involved in the initiation stage of the polymerization. Based on this assumption a kinetic equation in which K was a rate constant was deduced in well accordance with the experimental results: $R_p = KM^2C$.

Key words Double metal cyanide complex, Propylene oxide, Epoxides, Ring-opening polymerization, Kinetics