

·研究简报·

铁系催化剂催化降冰片烯与丙烯酸甲酯共聚合*

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摘 要 研究了 $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ (acac = 乙酰丙酮)催化降冰片烯(NB)与丙烯酸甲酯(MA)共聚反应条件影响、第三组份影响及催化剂铁铝比影响.并用核磁共振、红外光谱和元素分析方法研究了共聚物的组成,用热分析方法研究了共聚物的分解温度,并用电镜分析了共聚物的膜结构.结果表明,铁系催化剂在温和的反应条件下有较好的催化性能,并可获得能够形成有序多孔膜的共聚物.

关键词 乙酰丙酮铁, 三异丁基铝, 降冰片烯, 丙烯酸甲酯

降冰片烯与丙烯酸酯类共聚物是重要的光刻材料,目前该共聚物主要采用自由基聚合方法获得,如 Sharon^[1]等的原子转移自由基交替共聚合, Craford、Houlihan 和 Gu^[2~4]等的自由基聚合, Huang^[5]等用镍基催化剂获得了共聚物, Hreha^[6]等用自由基聚合方法获得降冰片烯与丙烯酸酯类均聚物.用铁系催化剂催化这类单体共聚报道较少见.我们在铁系催化剂催化丙烯酸酯类聚合^[7]、降冰片烯与马来酸酐共聚^[8]和马来酸酐与环氧化物共聚^[9]的基础上,将铁系催化体系用于降冰片烯与丙烯酸酯类共聚中,发现铁系催化剂催化共聚反应具有共聚物收率高、聚合速度快以及共聚物分子量分散较小等优点.本文考察了铁系催化体系催化降冰片烯(NB)与丙烯酸甲酯(MA)共聚反应的共聚合规律、共聚物结构、共聚物分子量和分子量分布以及共聚物成膜性能等.

1 原料及试剂

丙烯酸甲酯为化学纯,经5%氢氧化钠溶液洗涤和水洗、无水氯化钙干燥、氯化钙回流后,减压蒸馏精制备用,降冰片烯为英国 Lancaster 产品,甲苯为上海试剂一厂产品,分析纯试剂,用前经分子筛浸泡,三异丁基铝系瑞士 Fluka AG 产品,高纯氮系市售产品.

催化剂的配制和组成是在室温下,在单口聚合瓶中按比例加入乙酰丙酮铁,加入一定量的溶剂(0.03 g 乙酰丙酮铁及 1 mL 甲苯为溶剂)溶解

后,按比例加入三异丁基铝,即得红黑色催化剂溶液.实验中较好催化剂组成为乙酰丙酮铁:三异丁基铝 = 1:25(摩尔比).

2 聚合及聚合物分析

聚合操作在氮气氛中进行,采用真空抽烤充氮数次的单口聚合瓶,在瓶中加入溶剂、单体和催化剂,在恒温下聚合数小时后,加入含5%盐酸的甲醇溶液终止反应,聚合物用无水甲醇浸泡和洗涤,并真空干燥.核磁共振谱用 Bruker Avance DMX400 型核磁共振仪在室温下用三氯甲烷做溶剂测定,聚合物的红外光谱用 Paragon-1000 光谱仪测得.分子量用 Waters 1525 型凝胶渗透色谱仪,四氢呋喃作流动相测得,元素分析用 Thermo EA1112 元素分析仪测得.

3 共聚物的结构和性质

$\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ 催化降冰片烯与丙烯酸甲酯共聚,得到的产物为白色固体,可溶于氯仿、四氢呋喃,不溶于甲醇.图1是单体比为1:1时聚合物红外光谱,在 1738 cm^{-1} 处有羰基的吸收峰,说明聚合物中有丙烯酸甲酯单体,红外光谱在 1600 cm^{-1} 左右无吸收,说明聚合物中无碳碳双存在,证明了降冰片烯不是开环共聚.图2是单体比为1:1时的共聚物的核磁共振图谱,图中主要吸收峰能与共聚物结构单元中碳原子对应,1~4号峰主要是链节中丙烯酸甲酯的吸收峰,5~11号峰主要是链节中降冰片烯吸收峰,12号峰为溶剂

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三氯甲烷的吸收峰. 在相同实验条件下获得的丙烯酸甲酯均聚物¹³ C-NMR 图谱只在 174.9、51.7、41.3、35.4 处有吸收. 并且在共聚反应条件下降冰片烯不会均聚, 所以聚合物为 NB/MA 共聚物.

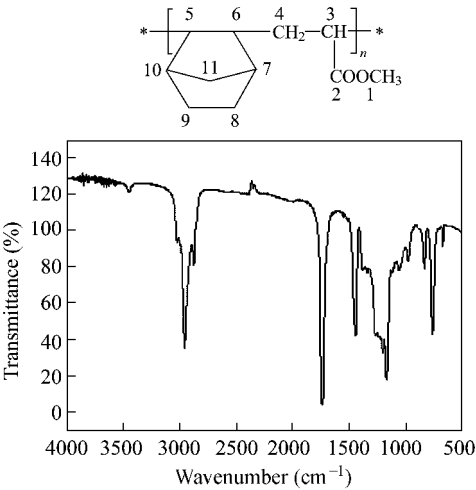


Fig. 1 Infrared spectrum of NB/MA copolymer

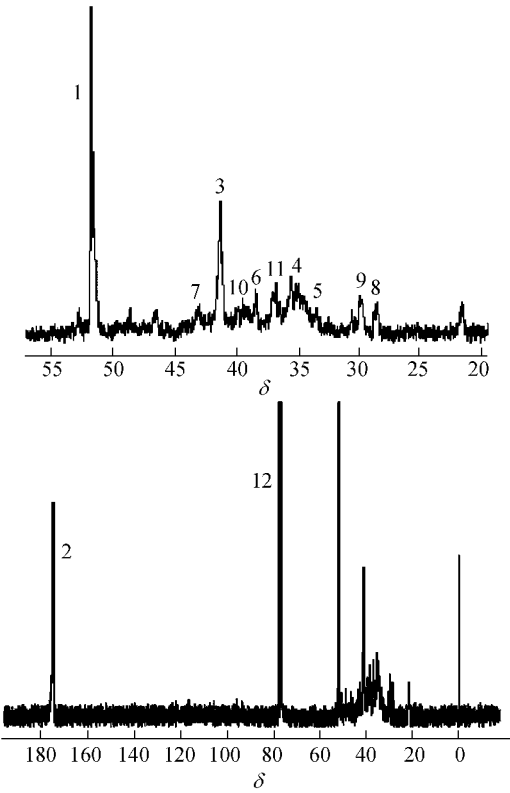


Fig. 2 ¹³C-NMR spectrum of NB/MA copolymer

表 1 列示了共聚物在不同单体摩尔比时分子量和分子量分布数据, 从表中数据可知, 分子量随着单体中降冰片烯摩尔比增加而下降, 分子量分布随着单体中降冰片烯摩尔比增加而变小. 用元素分析方法分析了不同单体比所获得的共聚物组

成, 从表中数据可知, 共聚物中降冰片烯含量不是很高, 共聚物中降冰片烯含量随单体中降冰片烯比例升高而增长.

Table 1 The Influence of monomer molar ratio on molecular weight and its distribution of copolymer

NB/MA (molar ratio)	Yield (%)	M_w	M_w/M_n	Copolymer composition (mol%)	
				f_{NB}	f_{MA}
1/2	47.7	1.05×10^5	2.67	12.3	87.7
1/1	37.9	5.82×10^4	2.44	19.5	80.5
2/1	17.0	5.19×10^4	2.25	26.0	74.0

Copolymerization conditions : 7 h, Al/Fe = 25 : 1 (molar ratio), [Fe] = 1.4×10^{-3} mol/L, Total monomer concentration = 5 mol/L, sol : toluene

4 共聚物热分析和膜的电镜分析

图 3 是共聚物的热分析图谱, 从谱图可见降冰片烯与丙烯酸甲酯共聚物的主要分解温度在 542℃, 并且峰形显示主要为一种聚合物的分解, 这与核磁共振图谱分析结果类似, 证明聚合物主要为共聚物.

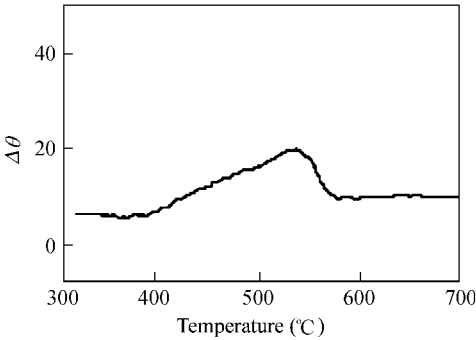


Fig. 3 DTA spectrum of NB/MA copolymer

图 4 是单体比为 1 : 1 时的聚合物四氢呋喃溶液采用提拉法制成的固体膜扫描电镜照片, 提拉方法为手工将玻片浸入溶液后提拉出凉干, 图中 mdan-1, mdan-2 为单次提拉形成的薄膜扫描电镜照片, mduo-3, mduo-4 为多次提拉形成的薄膜扫描电镜照片. 从电镜照片可以看到共聚物能够形成有序孔结构, 孔径大小在 7.0 ~ 15.0 μm 之间. 从电镜照片可以看到单次提拉形成的薄膜和多次提拉形成的薄膜形成的有序孔结构类似.

5 Fe-Al 体系催化降冰片烯与丙烯酸甲酯共聚特征

表 2 例示了反应温度对共聚合反应的影响, 从数据可知, 共聚反应随温度的升高共聚物的产率略有增长, 但增长不是很多, 说明反应温度对共聚反应影响不是很大.

表 3 例示了铁铝比对共聚的影响,数据表明在铁铝比为 1:10 ~ 1:150 之间对共聚的影响,总的趋势是随铝的比例上升共聚产物先上升后下降,这可能是随烷基铝的增加体系中水份减少收

率增加,但当烷基铝继续增加,使烷基铝链转移作用起主导时,则共聚物分子量变小,在甲醇中可溶部份增加,收率有所下降.

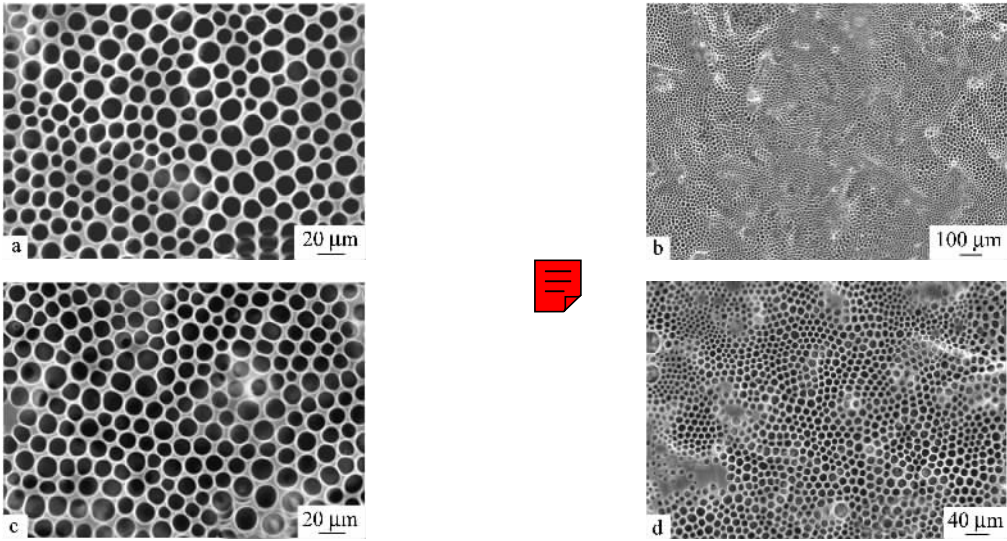


Fig. 4 SEM images of NB/MA copolymer films
a) mclan-1 ; b) mclan-2 ; c) mcluo-3 ; d) mcluo-4

Table 2 Influence of temperature on copolymerization				
Temperature (℃)	25	50	60	70
Yield (%)	29.9	30.9	35.1	37.9

Copolymerization conditions : 7 h, Al/Fe = 25:1 (molar ratio), NB/MA (molar ratio) = 1, [Fe] = 1.4 × 10⁻³ mol/L, the monomer molar ratio = 1:1, total monomer concentration = 5 mol/L, sol : toluene

Table 3 Influence of Fe/Al on copolymerization					
Fe/Al (molar ratio)	1:10	1:20	1:25	1:50	1:150
Yield (%)	17.8	21.2	37.9	11.7	7.8

Copolymerization conditions : 70℃, [Fe] = 1.8 × 10⁻³ mol/L, the monomer molar ratio = 1:1, total monomer concentration = 4 mol/L, sol : toluene

Table 4 Influence of third component on copolymerization	
Third component	Yield (%)
1,4-Dioxane	42.0
1,10-Phenanthroline	28.3
Carbon tetrachloride	43.2
8-Hydroxy quinoline	31.0
α, α'-Dipyridine	34.6
Tribenzylphosphine	38.3

Copolymerization conditions : 70℃, [Fe] = 1.4 × 10⁻³ mol/L, Al/Fe = 25:1 (molar ratio), the monomer molar ratio = 1:1, total monomer concentration = 5 mol/L, sol : toluene ; m (third component) / m (monomer) = 0.1%

表 4 例示了催化剂第三组份对共聚的影响,数据表明第三组份 1,4-二氧六环、四氯化碳和三苯膦对共聚的影响是使收率略有上升,其他第三组份使产率略有下降.这可能是由于带有吡啶环的第三组份对催化剂有络合作用,影响了催化剂对单体的作用,产率略有下降.

表 5 例示了加料顺序对共聚的影响,数据表明加料顺序以 NB + Sol. → MA → Cat. 收率最大,其他加料顺序收率都低于上述加料顺序.

Table 5 Influence of addition sequence on copolymerization	
	Yield (%)
NB + Sol. → MA → Cat.	37.9
NB + Sol. → Cat. → MA	29.8
MA → Cat. → NB + Sol	26.9
Cat. → MA → NB + Sol	30.3
Cat. → NB + Sol → MA	30.7

Copolymerization conditions : 70℃, [Fe] = 1.4 × 10⁻³ mol/L, Al/Fe = 25:1 (molar ratio), the monomer molar ratio = 1:1, total monomer concentration = 5 mol/L, sol : toluene

综上所述,铁系催化剂是降冰片烯与丙烯酸甲酯共聚较好的催化剂,具有聚合速度较快、产物收率较高等优点,共聚物形成的膜为有序多孔膜.

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COPOLYMERIZATION OF NORBORNENE AND METHYL ACRYLATE CATALYZED BY $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$

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Abstract The copolymerization of norbornene (NB) with methyl acrylate (MA) in the presence of iron (III) acetylacetonate [$\text{Fe}(\text{acac})_3$] associated with a triisobutylaluminum [$\text{Al}(i\text{-Bu})_3$] catalyst system was investigated. The polymerization was carried out under dry nitrogen in toluene in a glass flask equipped with a rubber septum. For preparing the catalyst system $\text{Fe}(\text{acac})_3$ was first dissolved in the reaction solvent, and $\text{Al}(i\text{-Bu})_3$ was then added. The monomers were first dissolved in the reaction solvent, and the catalyst was introduced to initiate the polymerization. After a given reaction time, the polymerization mixture was poured into a large amount of methanol containing a few percent of hydrochloric acid to precipitate the polymer. The liquid phase was filtered, and the recovered polymer was dried *in vacuo*. The characteristics of copolymerization of norbornene and methyl acrylate by $\text{Fe}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$ were studied. The copolymers were characterized by FTIR, ^{13}C -NMR, GPC and elementary analysis. Copolymers with NB content of 12.3 mol%, 19.5 mol% and 26.0 mol%, respectively were prepared. The molecular weight of the copolymers was in the range of $0.52 \times 10^5 \sim 1.05 \times 10^5$, and its distribution index M_w/M_n was in the range of 2.25 ~ 2.67. They both decreased with increasing the molar ratio of NB/MA. The copolymerization can be performed in the solvents such as aromatic hydrocarbons. The third composition could exert influence on the copolymerization. The yield of copolymers with a third composition like carbon tetrachloride or 1,4-dioxane and triphenylphosphine was higher than that of copolymers without the third composition. However, the addition of 1, 10-phenanthroline or 8-hydroxy quinoline and α, α' -dipyridine decreased the yield. The copolymerization could be obtained at room temperatures, however, increasing reaction temperature caused an increase of the copolymer yield. The yield of copolymer was also changed with the change of Al/Fe molar ratio, and the suitable Al/Fe molar ratio was 25. The copolymer can form porous membrane on cover glass automatically with pore size of 7 ~ 15 μm during evaporation of THF from the copolymer solution at room temperature.

Keywords Fe-Al Catalyst, Copolymerization, Norbornene, Methyl acrylate