

·研究简报·

从乙烯与丙烯酸二茂铁甲酰氧基乙酯共聚物制备碳纳米材料*

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摘 要 使用乙烯和丙烯酸二茂铁甲酰氧基乙酯(FcEA)为单体,合成了乙烯与丙烯酸二茂铁基乙酯共聚物 [P(E-co-FcEA)].以 P(E-co-FcEA)作为前驱体,通过改变裂解条件,自催化制得系列碳纳米材料.

关键词 二茂铁, 前驱体, 碳纳米材料

碳纳米材料(carbon nanomaterials)因在磁、电、光和力学等方面独特性能,使得它在纳米复合材料、纳米电子器件等多个领域得到了广泛应用,它的制备方法的研究是当今一个热点^[1].目前碳纳米材料如碳纳米管(CNTs)的制备方法主要有电弧放电法、激光蒸发法、水热法以及化学气相沉积法等,其中以化学气相沉积法最为简便易行,但用这种方法制备碳纳米材料通常需要有有机物作为碳源外,还要加入催化剂^[2],催化剂和碳源的接触或混合通常较难控制.二茂铁基聚合物具有很独特的性能,正受到很大的关注^[3~6].采用二茂铁基聚合物经自催化制备法来制备碳纳米材料能解决这个困难,这方面的研究正受到广泛的关注^[7~10].Keller^[7]报道了利用二茂铁乙炔基苯原位制备含纳米金属铁的碳纳米管,他们同时报道了利用二茂铁基化合物催化乙炔基苯类化合物也能生成碳纳米管^[8];Hempenius 发现对聚苯乙烯-*b*-聚二茂铁二甲基硅氧烷自组装的胶束进行热处理可获得纳米尺寸的催化剂,并以此可制得结构及

尺度可控的碳纳米材料^[9].本文尝试利用 α -二亚胺钨为催化剂催化乙烯与丙烯酸二茂铁甲酰氧基乙酯(FcEA)共聚,制得新型乙烯基二茂铁聚合物.并且以这种新型聚合物为前驱体,经自催化制备碳纳米材料.

碳纳米材料的合成路线如图 1 所示.乙烯与丙烯酸二茂铁甲酰氧基乙酯共聚物的制备在 25℃和 1.013×10^5 Pa 乙烯气体条件下制备(表 1).利用 ¹H-NMR 对聚合物进行表征(图 2),可以看出, $\delta = 4.81, 4.40, 4.22$ 处峰可归属为二茂铁茂环上的质子峰,而化学位移在 $\delta = 6$ 左右的双键碳原子上的质子峰消失,表明聚合物中没有不饱和的双键存在. $\delta = 2.30$ 处出现的峰为连接羰基的亚甲基碳上两个质子峰,说明 FcEA 单体已经聚合到聚合物的分子链上.而在 $\delta = 0.80 \sim 1.50$ 出现的系列峰归属于超支化聚乙烯甲基、亚甲基和次甲基质子.这些表明,聚合产物为乙烯与 FcEA 共聚物.

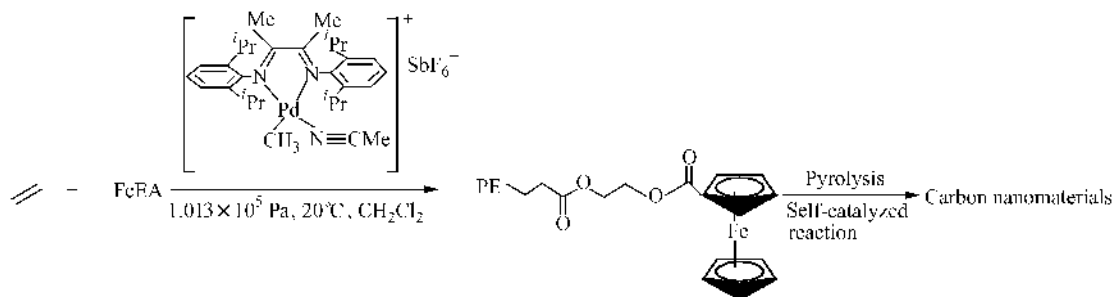


Fig. 1 Synthesis of carbon nanomaterials

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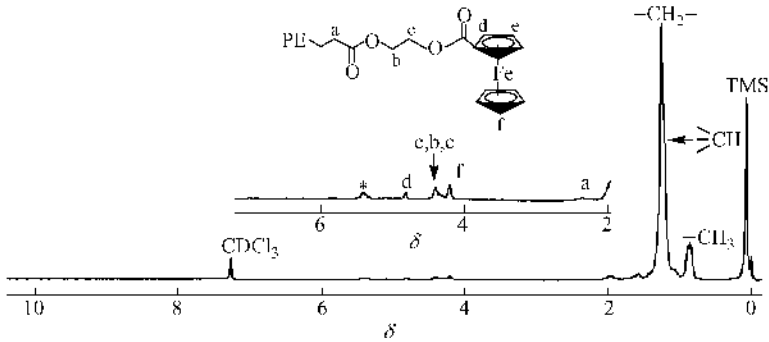


Fig. 2 ^1H -NMR spectrum of $\text{P}(\text{E-co-FcEA})$ ($\times \text{CH}_2\text{Cl}_2$)

Table 1 Conditions and results of copolymerization of ethylene and FcEA^a

Sample	Catalyst (mg)	[FcEA](mol/L)	Yield (g)	M_n	M_w/M_n	FcEA incorp (mol%)
HomoPE	8	0	1.8	119300	1.73	0
P(E-co-FcEA)-1	16	0.02	3.4	75100	1.57	0.03
P(E-co-FcEA)-2	16	0.05	3.0	63100	1.47	0.04
P(E-co-FcEA)-3	16	0.2	2.2	16400	1.52	0.08
P(E-co-FcEA)-4	16	0.4	0.6	2200	3.10	0.23

^aCompolymrization condition: Pd-diimine catalyst; Ethylene pressure, $1.013 \times 10^5 \text{ Pa}$; Polymerization temperature, 25°C ; Reaction time, 24 h; 20 mL CH_2Cl_2 as solvent

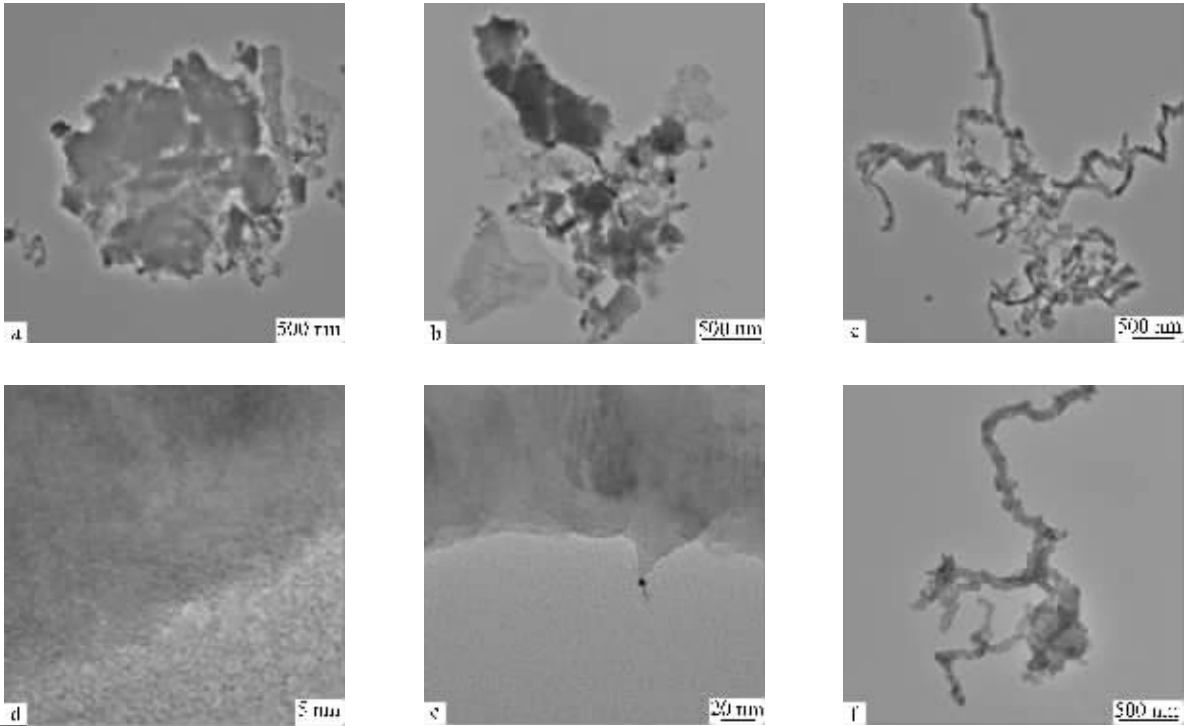


Fig. 3 TEM images of carbon materials

a), b) Amorphous carbon from the pyrolysis of $\text{P}(\text{E-co-FcEA})$ -1 and $\text{P}(\text{E-co-FcEA})$ -2 at 700°C , respectively; c) Carbon nanoropes from the pyrolysis of $\text{P}(\text{E-co-FcEA})$ -3 at 700°C ; d) Carbon layer; e) “↑” growing site; f) Carbon nanoropes from the pyrolysis of $\text{P}(\text{E-co-FcEA})$ -3 at 900°C

从制备的聚合物中极性单体的含量来看,聚合体系中极性单体含量越高,最后聚合产物中极性单体相应的也得到提高.如聚合体系中 FcEA 为 0.02 mol/L 时,聚合物中极性单体插入量只有 0.03 mol%,但聚合体系中 FcEA 为 0.4 mol/L 时,则提高到 0.23 mol%.从聚合产量来看,聚合体系中单体 FcEA 的含量对催化剂的活性影响很大,尤其是当单体 FcEA 的含量达到 0.4 mol/L 时,聚

合产量很低.同时 P(E-co-FcEA)-4 分子量很低,而且分子量分布很宽.比较其它丙烯酸酯类单体与乙烯共聚,我们认为 FcEA 含有二茂铁基团,体积较大,在共聚过程中具有较大的空间位阻效应^[11~13].

以 P(E-co-FcEA)为碳纳米材料为前驱体,而聚合物中的二茂铁为催化剂,经高温煅烧原位制备碳纳米材料^[14].在反应的过程中,聚合物前驱体裂解出 C 原子和 Fe 原子,Fe 原子融合形成 Fe 纳米颗粒,然后在 Fe 纳米颗粒的催化下,C 原子吸附在催化剂的表面而形成纳米碳层,进一步生长成碳纳米材料,图 3 是在不同的二茂铁的含量和煅烧温度时制得了碳材料.在 700℃下,较低含量二茂铁聚合物经煅烧 2 h 后(图 3a,b),发现产物中出现少量的纳米片(nanosheets).使用 P(E-co-

FcEA)-3 为前驱体,有大量的纳米绳(nanoropes)生成(图 3c),直径在 100 ~ 150 nm 之间.局部放大后,可以看到排列整齐的碳层,碳层间的距离为 0.34 nm(图 2d).同时在纳米绳的表面可以找到生长点(图 3e).如果将煅烧温度提高到 900℃,以 P(E-co-FcEA)-3 为前驱体,同样可以得到尺寸相当的碳纳米绳,表明温度对于碳纳米绳的生长影响不明显(图 3f).

综上所述,本文利用 α -二亚胺钯催化剂催化乙烯与丙烯酸二茂铁甲酰氧基乙酯(FcEA)共聚,制得了新型乙烯基二茂铁聚合物材料 P(E-co-FcEA),并以这种聚合物为前驱体,通过改变裂解条件和二茂铁在聚合中的含量,在高温下经自催化制备了新颖的碳纳米材料.

REFERENCES

- 1 Iijima S. Nature, 1991, 354(6348): 56 ~ 58
- 2 Benito A M, Maniette Y, Munoz E, Martinez M T. Carbon, 1998, 36: 681 ~ 683
- 3 Wang X J, Wang L, Wang J J, Chen T. J Phys Chem B, 2004, 108: 5627 ~ 5633
- 4 Chen T, Wang L, Jiang G H, Wang J J, Dong X C, Wang X J, Zhou J F, Wang C L, Wang W. J Phys Chem B, 2005, 109: 4624 ~ 4630
- 5 Zhou J F, Wang L, Dong X C, Tao C, Yang Q, Chen C, Chen X. Nanotechnology, 2006, 17: 2745 ~ 2751
- 6 Huo J, Wang L, Yu H J, Deng L B, Ding J H, Tan Q H, Liu Q Q, Xiao A G, Ren G Q. J Phys Chem B, 2008, 112: 11490 ~ 11497
- 7 Keller T M, Qadri S B. Chem Mater, 2004, 16: 1091 ~ 1097
- 8 Keller T M, Laskoski M, Qadri S B. J Phys Chem C, 2007, 111: 2514 ~ 2519
- 9 Hinderling C, Keles Y, Stockli T, Knapp H F, Acros T D L, Oelhafen P, Korczagin I, Hempenius M A, Vancso G J, Pugin R, Heinzelmann H. Adv Mater, 2004, 17: 14876 ~ 14879
- 10 Lu J Q, Kopley T E, Moll N, Roitman D, Chamberkin D, Fu Q, Liu J, Russell T P, Rider D A, Manner I, Winnik M A. Chem Mater, 2005, 17: 2227 ~ 2231
- 11 Chen G H, Huynh D, Felgner P L, Guan Z B. J Am Chem Soc, 2006, 128: 4298 ~ 4302
- 12 Johnson L K, Mecking S, Brookhart M. J Am Chem Soc, 1996, 118: 267 ~ 268
- 13 Szabo M J, Jordan R F, Michalak A, Piers W E, Weiss T, Yang S Y, Ziegler T. Organometallics, 2004, 23: 5565 ~ 5572
- 14 Chen Tao(陈涛). Study on the Synthesis, Self-assembly and Properties of Linear and Branched Ferrocene-Based Polymers(二茂铁基线性和支化聚合物的合成、自组装以及性能研究). Doctoral Dissertation of Zhejiang University(浙江大学博士论文), 2006

PREPARATION OF CARBON NANOMATERIALS WITH COPOLYMER OF ETHYLENE AND FERROCENYLFORMYLOXYETHYL ACRYLATE

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Abstract A novel copolymer, poly (ethylene-*co*-ferrocenylformyloxyethyl acrylate), P (E-*co*-FcEA), was synthesized from ethylene and ferrocenyl formyloxyethyl acrylate with an α -diimine palladium catalyst. The molecular weight and composition of the resultant copolymers were analyzed with gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR). The results suggested that the FcEA content in copolymerization system influenced not only the molecular weight, but also the composition of resultant copolymers. The molecular weight decreased dramatically with increasing FcEA contents. When the FcEA content was 0.02 mol/L in copolymerization system, the polar monomer content of the resultant copolymer was 0.03 mol% and $M_n = 75100$, while the FcEA content was 0.4 mol/L, the polar monomer content increased to 0.23 mol% and M_n was 2200. In addition, carbon nanomaterials were successfully prepared with P (E-*co*-FcEA) as precursor by self-catalyzed process, and the pyrolysis products were investigated with transmission electron microscope (TEM). Amorphous carbon containing a small amount of nanosheets was obtained using the copolymers containing 0.03 mol% and 0.04 mol% FcEA when the pyrolysis temperature was 700°C. Nevertheless, carbon nanowires were efficaciously prepared when FcEA content in copolymer was 0.08%. Moreover, increasing pyrolysis temperature to 900°C also afforded carbon nanowires.

Keywords Ferrocene, Precursor, Carbon nanomaterials