

有规立构聚苯乙烯的合成

许光学 卢泽俭 林尚安

(中山大学高分子研究所, 广州, 510275)

摘要 有规立构聚苯乙烯(等规、间规)作为一种具有潜在应用前景的高分子材料,已得到广泛重视和研究。本文收集 105 篇文献(到 1991 年 7 月)讨论有规立构聚苯乙烯的合成方法、聚合催化剂、聚合机理、聚合动力学和研究发展方向。

关键词 等规聚苯乙烯(IPS), 间规聚苯乙烯(SPS), 苯乙烯, 配位聚合, Ziegler-Natta 催化剂

1 引言

众所周知,聚合物的立体结构规整性对高聚物性能有很大影响,它决定聚合物晶体结构的类型和结晶度及其稀溶液、熔融态和固态物理性能,甚至常常还决定聚合物材料的工业应用(如聚丙烯)。因而控制聚合物立构规整性对开发新材料或“裁制”高聚物和控制聚合物的性能起着重要作用。早在 1929 年 H. Staudinger 提出大分子概念的同时,就曾预示聚合物立构规整性的重要性^[1]。直到 1954 年, Natta 等人^[2]用 Ziegler-Natta 催化剂在常压下合成等规聚丙烯后,有规立构聚合物的研究才有了较大突破。近几十年来, α -烯烃和二烯烃的定向聚合得到广泛研究且获得巨大进展,并已工业化^[3]。

有规立构聚苯乙烯(等规、间规)是重要的立构规整性聚合物。1955 年, Ziegler^[4]和 Natta^[5]分别用 AlEt_3 - TiCl_4 催化剂合成了等规聚苯乙烯(IPS), 而间规聚苯乙烯(SPS)直到 1986 年才由 Ishihara 等人^[6]用 TiCl_4 -MAO 催化体系在常温下合成得到。有规立构聚苯乙烯具有高熔融温度(IPS, $\sim 240^\circ\text{C}$; SPS, $\sim 280^\circ\text{C}$)、高结晶度、高热变形温度(IPS, $> 170^\circ\text{C}$; SPS, $> 240^\circ\text{C}$)、高拉伸强度、高模量以及优良的电绝缘性能和耐腐蚀性能。目前有规立构 PS 的研究方兴未艾,它们具有潜在应用前景,可作耐温和耐化学腐蚀工程塑料^[7]、绝缘材料^[8]、塑料合

金^[9]、功能纤维^[10]、分离膜^[11]、高性能泡沫材料^[12]和耐温薄膜^[13]等。本文就有规立构聚苯乙烯(IPS 和 SPS)的合成作一综述。

2 有规立构聚苯乙烯的合成

2.1 等规聚苯乙烯(IPS)的合成

早在 1950 年, Marton^[14]曾用“Alfin”催化剂得到了立构规整的聚苯乙烯,但当时并未引起注意。直到 1955 年 Ziegler^[4]和 Natta^[5]用 Ziegler-Natta 催化剂聚合出 IPS 才真正认识到。不过,“Alfin”型催化剂聚合苯乙烯的等规度和催化效率很低,聚合物难以抽提分级,已不再应用^[15]。对 IPS 的研究主要集中在寻找高等规度、高活性、高转化率的催化剂及其结构与性能及应用关系。迄今为止, IPS 的合成有配位聚合、阴离子和阳离子聚合。 t -BuOLi/BuLi 作为阴离子聚合催化剂合成 IPS 取得了进展^[16]。阴离子聚合 IPS 之优点为分子量易控制、分散指数低,而且易合成含 IPS 嵌段链的共聚物合金,



许光学 30 岁, 博士研究生。曾参与从事“863”科研项目“人工种子”的子项目“人工种皮”的研究, 现从事配位聚合和功能高分子材料的研究。先后发表学术论文 10 篇。

但催化效率、转化率和等规度不及 Ziegler - 剂有钛系^[5,17~23,26~33,35~37,49]、钒系^[24,25]、镍系^[48] Natta 配位聚合优越。制备 IPS 配位聚合催化 和稀土^[50]体系,如表 1 所示。

表 1 等规聚苯乙烯(IPS)聚合文献示例

作者	催化体系	溶剂	温度,℃	时间,h	转化率,%	催化效率 gPS/gTi 或 V	等规度,%	文 献
Natta(1955)	TiCl ₄ - Al(C ₂ H ₅) ₃	庚烷	70	7	43.7	38	结晶性	5,17
Williams(1958)	TiCl ₄ - Al(<i>i</i> - C ₄ H ₉) ₃	庚烷	70	24	72.0	51.8	等规	18
Overberger(1959)	TiCl ₄ - Al(<i>i</i> - C ₄ H ₉) ₃	庚烷	80	20	30.0	11.9	结晶性	19
Vandenberg(1960)	TiCl ₃ - Al(<i>i</i> - Bu) ₃	苯	60	4	58~80	22.5	93~94	20
Kern(1960)	TiCl ₄ - Al(C ₂ H ₅) ₃	庚烷	50	2~4	8.2~13.7	76.9~129	等规	21
Otto(1964)	TiCl ₄ - Al(C ₂ H ₅) ₃	苯	40	4	7.1	41.6	等规	22
Montecatini(1965)	TiCl ₃ - Al(C ₂ H ₅) ₃	环己烷	60	4	59.1	441.0	95	23
Montecatini(1965)	TiCl ₃ - Al(C ₂ H ₅) ₃	庚烷	60	4	40.1	75.3	92.6	23
Kapur(1967)	VOCl ₃ - Al(C ₂ H ₅) ₃	庚烷	40	3	20	17	30	24
Kapur(1968)	VOCl ₄ - Al(C ₂ H ₅) ₃	苯	40	1	2.1	7	40	25
Natta(1969)	TiCl ₄ - Al(C ₂ H ₅) ₃	庚烷	70	6	12	31.3	>95	26
Takashi(1970)	TiCl ₃ - AlEt ₃ - Et ₃ SbCl ₂	庚烷	50	1	—	386.5	1.5	27
Azuma(1970)	TiCl ₃ - 1/3AlCl ₃ - Et ₃ Al - H ₂ NCH ₂ CH ₂ OH	甲苯	70	3~5	61.7	4.6	83.8	28
Gude(1971)	TiCl ₄ - VOCl ₃ - AlEt ₃ - Et ₂ AlCl	甲苯	70	6	30	237.5	95	29
Koide(1976)	Ti[O - <i>n</i> - (C ₄ H ₉) ₂] ₄ - AlEt ₃	庚烷	60	20	24	15.2	85	30
Мардикин(1981)	TiCl ₄ - Al(C ₆ H ₁₃) ₃ • 1/3Mg(C ₆ H ₁₃) ₂	庚烷	70	4	28	51.7	80	31
Mardykin(1981)	TiCl ₄ - Al(C ₆ H ₁₃) ₃ • Mg(C ₆ H ₁₃) ₂	辛烷	70	4	28	13.3	85.7	32
Kashiwa(1985)	TiCl ₄ - MgCl ₂ - AlEt ₃	甲苯	50	0.5	—	420.8	84.2	33
Alberola(1986)	VCl ₃ - AlEt ₃	甲苯	50	1	90	89.7	60~70	34
L. Shangan(1986)	TiCl ₄ - MgCl ₂ - SiCl ₂ Ph ₂ - NdCl ₃ • <i>n</i> EtOH	苯	50	2	97	2300.0	98.5	35
L. Shangan(1987)	TiCl ₄ - NdCl ₃ - MgCl ₂ - AlR ₃	苯	50	2	81~97	1700~2400	95~98.8	36
Kashiwa(1987)	TiCl ₄ - MgCl ₂ - AlEt ₃ - EB	甲苯	50	0.5	40~50	165	90	37
Asanuma(1987)	TiCl ₄ - MgCl ₂ - Si(OEt) ₄ - Al(<i>i</i> - Bu) ₃	庚烷	70	2	37.0	>693	高等规度	38
Asanuma(1987)	TGY - AlEt ₃	甲苯	70	0.5	62	112	94.2	39
Asanuma(1988)	TiCl ₄ - MgCl ₂ - Si(OEt) ₄ - Al(CH ₂ CHMe ₂) ₃	庚烷	65	5	20.2~38.1	780~900	90~95	40
Kuramoto(1988)	TiCl ₄ - SiCl ₄ - Mg(OEt) ₂ - MAO	甲苯	50	2	70.1	33224.0	14.1	41
Kakugo(1988)	TiCl ₄ - MAO - MgR ₂	甲苯	50	14	17.9	77.4kg /Ti 原子	结晶性	42
Soga(1988)	TiCl ₃ - CpTiMe ₂	庚烷	40	1	25.1	10.6	99.2	43
Soga(1988)	TiCl ₄ - MgCl ₂ - AlEt ₃ - EB	庚烷	40	1	18.1	423.1	80.2	43
Soga(1989)	TiCl ₄ - MgCl ₂ - CpTiMe ₂ - EB	庚烷	40~60	1	20~40	650.0	98.6	44
Soga(1989)	Ti(acac) ₃ - MgCl ₂ - Et _{1.5} AlCl _{1.5} - CpTiMe ₂	庚烷	40~60	1	20~50	400.0	~100	45

续表 1

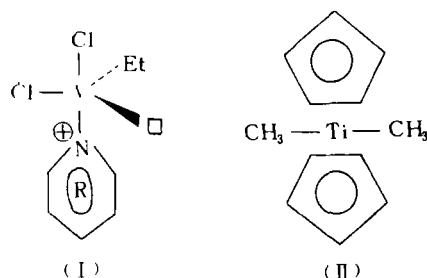
作者	催化体系	溶剂	温度, °C	时间, h	转化率, %	催化效率 gPS/gTi 或 V	等规度, %	文献
Gaponik(1989)	$\text{TiCl}_4 - (\text{C}_7\text{H}_{15})\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	庚烷或 辛烷	70	4	28~53	69.3	83.4	46
Soga(1990)	$\text{Ti}(\text{OC}_4\text{H}_9)_4 - \text{Mg}(\text{OH})\text{Cl} - \text{AlMe}_3$	庚烷	40	24	—	0.4	~100	47
Soga(1990)	$\text{TiCl}_4 - \text{MgCl}_2 - \text{EB} - \text{AlEt}_3$	庚烷	40	0.5	—	414	93.4	47
Soga(1990)	$\text{TiCl}_3 - \text{MgCl}_2 - \text{AlEt}_3$	庚烷	40	0.5	—	65	96.7	47
Longo(1990)	$\text{Ni}(\text{acac})_2 - \text{MAO}/\text{Et}_3\text{N}$	甲苯	25	25	30.7	1446gP/gNi	40	48
Yamada(1990)	$\text{TiCl}_3 - \text{AlEt}_3 - \alpha - \text{cyclodextrin}$	甲苯	70	2	66.1	2127.6	93.2	49

钛系催化剂由于聚合活性高且产物等规度高诸特点而占有主导地位。另外,钛系催化剂的物理形态较易控制,而催化剂的物理形态恰恰是决定 IPS 立构规整性^[5]、催化效率^[6]、聚合物微观形态^[3]和粒度及表观堆密度^[3]的一个重要因素。镍系催化剂能有效控制 IPS 分子量分布,较钛系理想(如 Ti : $\bar{M}_w/\bar{M}_n \geq 11$; Ni : $\bar{M}_w/\bar{M}_n = 1.4 \sim 4.2$)^[48]。Natta 研究发现苯乙烯等规聚合的另一特点是只有非均相 Ziegler-Natta 催化剂才能合成高等规度 IPS^[3,17],后续研究证实这一观点^[12,35,36,44,45,47]。苯乙烯等规聚合过程中, TiCl_3 和 TiCl_4 母体催化剂的立体定向选择性差异不如丙烯聚合显著,这与苯乙烯单体性质有关^[17]。由于苯乙烯的芳环能与催化剂活性中心络合而失活,因此 IPS 聚合的催化效率比其它 α -烯烃要低^[51]。

苯乙烯等规聚合动力学研究表明,单体转化率、催化效率、聚合物等规度和分子量及其分布取决于催化剂组成^[28,29,32,35,37,41,45]、催化剂陈化时间^[34,46,47,52]、催化剂浓度^[36,43]、Al/Ti 比^[19,36]、聚合温度^[19,26,36,44~46]、聚合时间^[21,33,37]、溶剂^[23]、搅拌速度^[32,46]和烷基铝性质及浓度^[3,25,26,36,46,52]。

提高 IPS 的等规度是近年来研究的中心内容。Mardykin 等人^[53]在催化剂中引入电子给予体(如醚)提高了催化剂体系对苯乙烯聚合立体定向性,而且等规度随着聚合时间而增大。Kashiwa^[37]在催化剂中引入苯甲酸乙酯(EB)也得到相同结论,并认为 EB 抑制或减慢了等

规活性中心的衰减,相对加快了非定向活性中心失活。近来研究认为,EB 有助于提高等规度主要在于它具有毒化等规性低的活性中心^[54]、提高活性中心等规性^[55,56]和提高等规活性中心的 Kp 值^[56]等特性。对于钒体系催化剂,Alberola^[34]发现加入杂环碱(如吡啶)有利于提高 IPS 等规度。据认为是杂环碱与催化剂配位形成较高定向选择性的等规活性中心(I)所致。

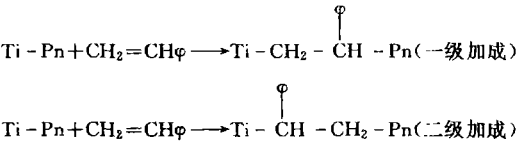


最近, Soga^[43,44]在提高 IPS 等规度方面取得有意义结果,他发现二甲基二茂钛(Cp_2TiMe_2)(II)作为助催化剂加到钛系母体催化剂中可大大提高 IPS 等规度(几乎达 100%)。这是由于 Cp_2TiMe_2 的存在使无规活性中心很容易转化为等规活性中心所致^[57],但大多数潜在的活性中心仍未被活化,故催化活性仍较低。

苯乙烯等规聚合过程中,如何解决等规度和催化效率及转化率这对矛盾仍需进一步研究,这是 IPS 的催化剂研究方向。有意义的是,我们在钛系母体催化剂中加入稀土钨化合物得到的 SN-1 催化剂具有高活性、高等规度、高

转化率和高聚合速率及高分子量等综合特点^[35,36]。而且 SN-1 催化剂还具有较高的苯乙烯-α-烯烃共聚活性^[58],这与 SN-1 催化剂活性中心结构和浓度以及聚合机理有关^[36]。

有规立构聚苯乙烯加成方式主要有一级加成和二级加成两种:



¹³C NMR 对苯乙烯等规聚合链增长机理研究表明^[34,59],链增长加成机理随催化剂性质而定。非均相钛系催化剂进行苯乙烯等规聚合时,与其它 α-烯烃聚合一样^[60],单体顺式插入活性中心 Ti-C 键按一级加成机理进行链增长。而镍催化剂则是按二级加成机理进行链增长,同时链增长过程中往往伴随活性中心构型改变

而引起产物立构规整性变化^[48]。此外,动力学研究表明^[46],对单体而言,苯乙烯等规配位聚合属二级反应,但对催化剂而言属一级反应。

2.2 间规聚苯乙烯(SPS)的合成

在低温下(-65℃)用自由基引发剂或 Ziegler-Natta 催化剂来合成 SPS 早有报道^[61,62],但效率和间规度都相当低。1986 年, Ishihara^[6]首次发现 TiCl₄ 或 CpTiCl₃-MAO 催化剂体系能合成高间规度和结晶度的 SPS,而且还具有高的催化效率和单体转化率。近几年来,在 Ishihara 工作的基础上,开发合成 SPS 的催化剂、研究聚合特性、结构与性能以及加工应用诸方面已取得较大进展。合成 SPS 的催化剂主要为 Ti 系^[6,63~69,71~76,80~96]和 Zr 系^[65,70,77,79]两类,其中 Ti 系占主导地位,如表 2 所示。

表 2 间规聚苯乙烯(SPS)聚合文献示例

作者	催化剂体系	溶剂	温度 ℃	时间 h	转化率 %	催化效率 gPS/gTi 或 Zr	间规度 %	参考文献
Ishihara(1986)	TiCl ₄ -MAO	甲苯	50	2	97.6	—	>98	6
Ishihara(1987)	CpTiCl ₃ -MAO	甲苯	20	1	97	—	96	63
Ishihara(1987)	TiCl ₄ -MAO	甲苯	20	1	7.7	2916.7	≥90	64
Pellecchia(1987)	Ti(C ₆ H ₅ CH ₂) ₂ 或 Zr(C ₆ H ₅ CH ₂) ₂ -MAO-AlEt ₃	甲苯	60	1	5	390.6	97	65
Kakugo(1987)	Complex of DHDTBDMPS 和 TiCl ₄ 或 (i-PrO) ₄ Ti-MAO	甲苯	—	—	—	高活性	>99	66
Albizzati(1988)	TiCl ₃ N(Et) ₂ -MAO	甲苯	50	4.5	25	1894.5	86	67
Soga(1988)	Ti(SO ₄) ₂ ·4H ₂ O-MAO	甲苯	40	48	—	4460	98	68
Ishihara(1988)	(η-C ₅ H ₅)TiCl ₃ -MAO	甲苯	50	2	68~99.2	8597	≥99	69
Albizzati(1988)	Zr(CH ₂ Ph) ₄ -MAO	甲苯	50	4.5	20	5449.5	23	70
Albizzati(1988)	Ti(OBu) ₄ -MAO	甲苯	50	4.5	59	2487.1	93	71
Ishihara(1988)	Ti(OEt) ₄ -MAO	甲苯	40	1.5	7.5	4166.7	98	72
Imayoshi(1988)	Cp ₂ TiCl ₂ -MAO	甲苯	50	6	—	>2500	≥99	73
Imayoshi(1988)	Cp ₂ TiCl ₂ -MAO-AlR ₃	甲苯	50	6	—	>4000	≥99	74
Imayoshi(1988)	Cp ₂ TiCl ₂ -MAO-AlMe ₃	甲苯	50	6	20	8000	≥99	75
Nakano(1988)	Ti(OEt) ₄ -MAO	甲苯	—	8	—	—	100	76
Campbell(1988)	Zr(OPr) ₄ -MAO	Isopar E	51	40	1.6	10~109.6	>75	77
Campbell(1988)	CpTi(OC ₆ H ₅) ₃ -MAO	Isopar E	51	20	96.9	6305.8	>95	78
Schmidt(1989)	CpZrCl-MAO	Isopar E	50	20	—	6500	≥65	79
Tomotsu(1989)	Me ₅ CpTi(OCH ₃) ₃ -MAO- 乙二醇	甲苯	70	1	21.5	3392.4	96	80
Maezawa(1989)	CpTiCl ₃ -MAO	甲苯	50	1	32.1	4166.7	98	81
Maezawa(1989)	CpTiCl ₃ -MAO-AlMe ₃	甲苯	50	1	80	10400	98	82

续表 2

作者	催化剂体系	溶剂	温度 ℃	时间 h	转化率 %	催化效率 gPS/gTi 或 Zr	间规度 %	参考 文献
Kuramoto(1989)	CpTiCl ₃ - MAO - α 氧化铝	甲苯	50	—	70	—	98	83
Zambelli(1989)	Ti(bz) ₄ - MAO	甲苯	50	1.5	6~20	683.3	93	84
Soga(1989)	Ti(OBu) ₄ - MAO	甲苯	25	3	2	30.2	100	85
Soga(1989)	Ti(SO ₄) ₃ · 8H ₂ O - AlMe ₃	甲苯	40	48	—	—	>98	86
Soga(1990)	Ti(OBu) ₄ - MAO - SiO ₂	甲苯	40~90	1	—	71.9~563.1	100	87
Soga(1990)	Ti(O - <i>n</i> - Bu) ₄ /Mg(OH) ₂ - MAO	甲苯	27	19	4.5	84.4	~100	88
Imabayashi(1990)	(Me) ₅ CpTi(OCH ₃) ₃ - MAO - Al(<i>i</i> - Bu) ₃	甲苯	75	2	28	128.84 kg P/gTi	98	89 (连续生产工艺)
Arai(1990)	CpTi(OEt) ₃ - MAO	甲苯	50	0.25	65.9	12500	≥99	90
Tsuruta(1990)	CpTiCl ₃ - MAO - 二(2-甲氧苯基)苯膦或二(2-羟苯基)苯膦	甲苯	60	1	11.2	2120	98	91
Imayoshi(1990)	Ti(OPr - <i>i</i>) ₄ - MAO	甲苯	80	4	22.9	7.3	33.5	92 (气相聚合)
Yamamoto(1990)	(Me) ₅ CpTi(OCH ₃) ₃ - MAO - Al(<i>i</i> - Bu) ₃	甲苯	75	2~5	30~70	132.7 kg P/gTi	98	93
Takeuchi(1990)	(Me) ₅ CpTi(OCH ₃) ₃ - MAO	甲苯	70	4	28.8	435.8	98	94
Tazaki(1990)	(Me) ₅ CpTi(OCH ₃) ₃ - AlEt ₂ H - MAO	甲苯	70	1	25.1	11900	98	95
Hirakawa(1990)	Ti(OBu) ₄ - MgCl ₂ - Si(HRO) _n - MAO(<i>n</i> ≥2)	甲苯	40	1	11.8	—	≥96	96 (高结晶度)
Chien(1991)	CpTi(OBu) ₃ /MAO	甲苯	60	1	94	104000	99	97
Ishihara(1991)	(C ₆ H ₅) ₂ Ti/MAO	甲苯	50	4	—	(高活性)	>90	98

合成 SPS 的催化剂多数是均相可溶 Kaminsky 型催化剂。Ishihara^[69]研究表明,只有 Ti 系催化剂才能合成纯 SPS,而 V 系和传统的 Kaminsky 催化剂[(η - C₅H₅)₂ZrCl₂ - MAO]得不到纯 SPS 产物。类似的 Ni 系催化剂只能合成 IPS^[48],Nb、Ta、Cr 和 Co 系根本不能合成有规立构 PS^[69]。Soga^[68,88]对 Ti 系和 Zr 系等催化剂的研究支持了 Ishihara 的结论。虽有少数 Zr 化合物可合成 SPS,但效果欠佳^[65,70,77,79]。Ti 系催化剂中 Ti 的价态、配体性质和大小对合成 SPS 有一定影响^[69,84]。含茂基配体的 Ti 系催化剂效果最为理想。Ishihara^[69]比较了各种 Ti 化合物的催化活性得到如下顺序: CpTiCl₃ ~ Cp* TiCl₃ (Cp* 为 η^5 - pentamethylcyclopentadienyl) ≥ CpTiClH ~ Ti(OEt)₄ > Ti(OMe)₄ ~ TiCl₄ > TiBr₄。

苯乙烯间规聚合与烷基铝的性质^[6,65,68,69,88]和浓度以及 Al/Ti 比有密切关系。只有 MAO 作助催化剂才能制备 SPS^[69],而其

它有机铝化合物效果极差。MAO 的存在有助于间规活性中心的形成^[99],同时还可以阻止或延缓催化剂活性种的失活^[100,101]。此外,聚合温度^[87,97,102]和聚合时间^[97,102]对苯乙烯间规聚合速率、催化效率和单体转化率也有影响。

合成 SPS 的催化剂除主要是 Kaminsky - Sinn 型外^[88],最近还报道了异相载体催化剂。催化剂活性和苯乙烯间规聚合特性主要取决于载体类型和性质。Kuramoto 等人^[83]用 Al₂O₃ 作载体可提高单体的转化率或产率。Soga^[87]用 SiO₂ 作载体的 Ti(OBu)₄/MAO/SiO₂ 催化剂热稳定性好,形成单一活性中心,有效提高催化效率和间规度,同时产物分子量分布窄;而用于丙烯聚合时,得到聚丙烯分子量分布则较宽^[103]。这再次表明苯乙烯和丙烯间规聚合机理上的差异。值得注意的是,Mg 化合物作载体时,苯乙烯有规立构聚合和催化效率与 Mg 的配体有关,含氯原子配体的 Mg 化合物载体有利于等规聚合,而只有非氯原子配体 Mg 化合

物[如 $\text{Mg}(\text{OH})_2$]载体才能合成 SPS。载体金属的配体对有规立构苯乙烯聚合的作用机理以及高效载体催化剂的开发有待进一步研究。

苯乙烯间规聚合机理尚未有圆满模型提出。Zambelli 等^[104,105]用 ^{13}C -NMR 研究 SPS 产物的末端结构,发现单体全部是以二级加成方式增长的,并认为二级加成插入是间规聚合的一个共同特点,链增长过程中伴随 β -脱氢反应进行链转移而发生链终止。Soga^[57]用制得 SPS 的 $\text{Ti}(\text{OBu})_4/\text{MAO}$ 催化剂进行苯乙烯共聚合,发现一些通常易进行共聚合的烯烃单体却不聚合,而阳离子聚合活性较高的茚却易与苯乙烯共聚,这说明苯乙烯间规聚合可能是阳离子聚合的机理。最近 Zambelli^[99]的研究支持阳离子聚合机理的观点。

总之,合成 IPS 和 SPS 的研究仍将集中在开发高活性、高等规度、高转化率、高聚合速率的新型催化剂,同时从理论上探讨催化剂组分的作用、活性中心结构与性质、聚合反应机理和 IPS 或 SPS 结构与性能及其应用的关系,从而开发出 PS 新型高分子材料或合金。

3 参考文献

- 1 Staudinger H. Effect of Stereoregularity on crystallizability of polymers. *Helv. Chim. Acta*, 1929, 12(2): 934~940
- 2 Natta G, Pino P and Porradini P. Crystalline high polymers of α -olefins. *J. Am. Chem. Soc.*, 1955, 77(6): 1708~1710
- 3 Boor J Jr. Ziegler-Natta catalysts and polymerization. New York: Academic Pr, 1979
- 4 Ziegler K, Montecatini H. Catalysts of α -olefins' polymerization. *Belg. Pat.*, 543259, 1955
- 5 Natta G. Polymerization of crystalline PS. *J. Polym. Sci.*, 1955, 16(1):143~147
- 6 Ishihara N, Seimiya J and Uoi M. Crystalline syndiotactic PS. *Macromolecules*, 1986, 19(9):2464~2465
- 7 Tjitsu T, Sumitomo T and Sawada M. Heat- and impact-resistant styrene-based resin. *Eur. Pat. Appl. EP*, 318 793, 1989
- 8 Ito T, Tsunashima K and Yabe K. PS films for electrical insulation. *Jan. Kokai Tokkyo Koho*, JP 6261202, 1987
- 9 Kuramoto M, Nakano A, Suzuki M and Sawada M. Heat-resistant and tough PS compositions. *Jan. Kokai Tokkyo Koho*, JP 62257948, 1987
- 10 Pedersen D R. Manufacture of stereoregular polystyrene fibers. *Eur. Pat. Appl. EP* 356856, 1990
- 11 Beck H N, Mahoney R D. Manufacture of microporous membranes from IPS-SPS blends. *US* 4927535, 1990
- 12 Sumitomo K. Thermoplastic polystyrene foams and their manufacture. *Jan. Kokai Tokkyo Koho*, JP 02248438, 1990
- 13 Imayoshi M, Arai T. Syndiotactic styrene polymer films. *Jan. Kokai Tokkyo Koho*, JP 01168709, 1989
- 14 Marton A A. Polymerization of styrene with Alfin catalysts. *Ind. Eng. Chem*, 1950, 42(4): 1488~1492
- 15 Williams R. Crystallizable polystyrene. II. Polymerization of styrene with triphenylmethyl potassium and related compounds. *J. Org. Chem*, 1958, 23(4):638~640
- 16 Luigi C, Cohen R E. Anionic synthesis of isotactic PS. *Macromolecules*, 1989, 22(10):4125~4128
- 17 Natta G, Danusso F. Polymerization of styrene and its derivatives. *Makromol. Chem*, 1958, 28(2):253~257
- 18 Williams R L J. Crystallizable polystyrene; III. A comparison of crystallinities of polystyrenes prepared using various catalysts. *J. Org. Chem*, 1958, 23(8):1206~1208
- 19 Overberger G C, Ang F and Mark H. A convenient laboratory preparation of isotactic PS. *J. Polym. Sci*, 1959, 35(129):381~389
- 20 Vandenberg J E. Polymerization of styrene. *US* 2954367, 1960
- 21 Kern R J, Hurst H G and Richard W R. Triethylaluminum-titanium tetrachloride catalysts for preparation of crystalline PS. *J. Polym. Sci*, 1960, 45(145):195~204
- 22 Otto F D, Parravano G. Polymerization of styrene with TiCl_3 - $\text{Al}(\text{C}_2\text{H}_5)_3$ and VCl_3 - $\text{Al}(\text{C}_2\text{H}_5)_3$ catalysts. *J. Polym. Sci., Part A*, 1964, 2(12):5131~5147
- 23 Anand C L, Kapur L S. Polymerization of styrene with VOCl_3 -aluminum alkyls. *J. Polym. Sci., Part A-1*, 1967, 5(8):2079~2089
- 24 Anand C L, Kapur L S. Polymerization of styrene with VCl_4 -aluminum alkyls. *J. Polym. Sci., Part A-1*, 1968, 6(4):909~918
- 25 Montecatini A P S E. Polystyrene. *Ital. Pat.*, 696064, 1965
- 26 Natta G, Pino P and Mazzanti G. Isotactic PS and poly-

- 1-pentene. US, 3435018, 1969
- 27 Takashi Y, Aijima I and Tsunoda Y. Polymerizing α -olefins utilizing a novel ternary catalyst. US, 3494910, 1970
 - 28 Azuma H, Nanikawa S. Polymerization of ethylene, propylene and styrene by use of activated Ziegler catalyst. Jan. Kokai Tokkyo Koho, JP. 70-15986, 1970
 - 29 Gude F. Crystalline styrene polymers. Ger. Offen. 2020885, 1971
 - 30 Koide N, Takede M. Ionic polymerization. New York: Academic Pr, 1976
 - 31 Мардикин В П, Антипова А М, Гапоник Л В. Высоком. Соед., (B) 1981, 23(1):52~57
 - 32 Mardykin V P, Gaponik L V. Alkylaluminum magnesium complexes as components of a coordination catalyst of styrene polymerization. Vysokomol. Soedin., Ser. B, 1981, 23(1):52~54
 - 33 Kashiwa N. Olefin polymerization with magnesium chloride - supported titanium tetrachloride catalyst system. Polym. Prepr., 1985, 26(2):370~371
 - 34 Alberola A, Benito Y. Polymerization of styrene using triethylaluminum - vanadium trichloride. Eur. Polym. J., 1986, 22(4):323~325
 - 35 林尚安, 陆耘, 赵振河, 周新华, 卢泽俭. 高活性苯乙烯立体定向聚合催化剂. 中国发明专利申请公开说明书, CN 85102292, 1986
 - 36 周新华, 赵振河, 陆耘, 林尚安. 含稀土钛系催化剂的苯乙烯高活性定向聚合研究. 高分子学报. 1987, 4:265~270
 - 37 Kashiwa N, Yoshitake J and Tsutsui T. Polymerization of styrene with a highly active $MgCl_2$ supported $TiCl_4$ catalyst system. Polym. Commun., 1987, 28(2): 292~296
 - 38 Asanuma T, Takeda J. Viscosity - controlled polymerization of aromatic vinyl compounds, Jan. Kokai Tokkyo Koho, JP. 62-277410, 1987
 - 39 Asanuma T, Takeda J. Catalysts for manufacture of highly crystalline PS. Jan. Kokai Tokkyo Koho, JP. 62-174212, 1987
 - 40 Asanuma T, Takeda J. Purification of isotactic PS with acetoacetate esters and alcohols. Jan. Kokai Tokkyo Koho, JP. 63-75011, 1988
 - 41 Kuramoto M, Ishihara N and Nakano A. Process for preparing styrenic polymers. PCT Int. Appl. WO, 88-03540, 1988
 - 42 Kakugo M, Miyatake T and Mizunuma K. Catalysts for polymn of vinyl - aromatic compounds with high molecular weight. Jan. Kokai Tokkyo Koho, JP. 63191811, 1988
 - 43 Soga K, Yanagihara H. Synthesis of highly IPS by using Solvay - type titanium trichloride in combination with dicyclopentadienyldimethyltitanium. Makromol. Chem. Rapid Commun., 1988, 9(1): 23~25
 - 44 Yanagihara H, Soga K. Ziegler catalysts for the manufacture of IPS polymers. Jpn. Pat, 01254707, 1989
 - 45 Yanagihara H, Soga K. Ziegler catalysts for the manufacture of isotactic styrene polymers. Jpn. Pat, 01254708, 1989
 - 46 Gaponic V L, et al. Higher aluminum trialkyls and magnesium aluminum alkyls as components of Ziegler - Natta catalysts. J. Appl. Polym. Sci, 1989, 38(11):1975~1985
 - 47 Soga K, et al. Polymerization of styrene with heterogeneous Ziegler - Natta catalysts, Makromol. Chem., Rapid Commun., 1990, 11(5):229~232
 - 48 Longo P, Grassi A. Some ^{13}C NMR evidence on isotactic polymerization of styrene. Makromol. Chem., 1990, 191(1):237~242
 - 49 Yamada K, Machama S and Ozuru M. Polymerization catalysts for preparing IPS. Jpn. Pat, 02158608, 1990
 - 50 Yang M, Cha C and Shen Z. Polymerization of styrene by rare earth coordination catalysts. Polym. J., 1990, 22(10):919~923
 - 51 Boor J. Spec. Lect., Int. Congr. Pure Appl. Chem., 23rd 1971, Butterworths, London, 8, 57
 - 52 Sehra C J, Gundiah S. Kinetics of polymn. of styrene with butoxytitanium trichloride and diethylaluminum chloride. Makromol. Chem., 1984, 185(11):2283~2289
 - 53 Mardykin V P, Antipova M A. Effect of EB on polymerization of styrene. Vysokomol. Soedin., A, 1969, 11(5), 1600~1606
 - 54 Kashiwa M, et al. Olefin Polymn. with magnesium chloride - supported titanium tetrachloride catalyst system. Polym. Prepr., 1985, 26(2): 370~371
 - 55 Kashiwa M. Polymerization of olefins. J. Polym. Sci., Part C, 1984, 22: 2641~2648
 - 56 Soga K. Influence of $SeOCl_2$ on the polymerization of prepylene by $TiCl_3 - AlEt_3$. J. Polym. Sci., Part A-1, 1967, 5(11): 2815~2823
 - 57 Soga K, et al. Perfect conversion of aspecific sites into isospecific sites in Ziegler - Natta catalysts. Macromolecules. 1989, 22(9):3824~3826

- 58 卢泽俭, 陆耘, 林尚安. 含稀土钛系催化剂的乙烯/苯乙烯共聚合研究. 高分子学报. 1988(4): 268~273
- 59 Ammendola P, Tancredi T and Zambelli A. Isotactic polymerization of styrene and vinylcyclohexane in the presence of a ^{13}C -enriched Ziegler-Natta catalyst: Regioselectivity and enantioselectivity of the insertion into metal-methyl bonds. *Macromolecules*, 1986, 19(2): 307~310
- 60 Shelden A R, et al. Polymerization of α -olefins. *J. Polym. Sci., Part A*, 1965, 3(1): 23~27
- 61 Natta G, Pasquon I and Zambelli A. Stereospecific catalysts for the head-to-tail polymerization of propylene to a crystalline syndiotactic polymer. *J. Am. Chem. Soc.*, 1962, 84(8): 1488~1490
- 62 Doi Y, Suzuk S and Soga K. Crystalline syndiotactic olefin polymers. *Macromolecules*, 1986, 19(1): 289~290
- 63 Ishihara N, Kuramoto M and Uoi M. Preparation of syndiotactic polymers of styrene and styrene derivatives. *Eur. Pat. Appl. EP*, 210615, 1987
- 64 Ishihara N, Kuramoto M and Uoi M. Catalysts for manufacture of syndiotactic PS. *Eur. Pat. Appl. EP*, 224097, 1987
- 65 Pellicchia C, Longo P and Grassi A. Synthesis of highly syndiotactic PS with organometallic catalysts and monomer insertion. *Makromol. Chem., Rapid Commun.*, 1987, 8(6): 277~279
- 66 Kakugo M, Miyatake T and Mizunuma K. Novel homogeneous titanium catalysts for the preparation of SPS. *Chem. Express*, 1987, 2(7): 445~448
- 67 Albizzati E, et al. Manufacture of crystalline vinyl aromatic polymers having a predominantly syndiotactic structure. *Eur. Pat. Appl. EP*, 271874, 1988
- 68 Soga K, Shiano T. Polymerization of styrene with the catalyst system prepared from hydrated transition metal (Ti, Zr) compounds and trimethylaluminum. *Makromol. Chem., Rapid Commun.*, 1988, 9(5): 351~354
- 69 Ishihara N, Kuramoto M and Uoi M. Stereospecific polymerization of styrene giving the syndiotactic PS. *Macromolecules*, 1988, 21(12): 3356~3360
- 70 Albizzati E, et al. Process and catalysts for producing crystalline vinyl aromatic polymers having a predominantly syndiotactic structure. *Eur. Pat. Appl. EP*, 272584, 1988
- 71 Albizzati E, et al. Manufacture of crystalline syndiotactic vinyl aromatic polymers. *Eur. Pat. Appl. EP*, 271875, 1988
- 72 Ishihara N, Kuramoto M and Uoi M. Process and catalysts for manufacture SPS. *Eur. Pat. Appl. EP*, 275943, 1988
- 73 Imayoshi M, Arai T and Tsuyama S. Manufacture of stereospecific PS. *Jpn. Pat.*, 63-268709, 1988
- 74 Imayoshi M, Arai T and Tsuyama S. Manufacture of SPS. *Jpn. Pat.*, 63-268710, 1988
- 75 Imayoshi M, Arai T and Tsuyama S. Stereospecific PS. *Jpn. Pat.*, 63-268711, 1988
- 76 Nakano A, et al. Styrene polymer moldings with improved mechanical strength. *Jpn. Pat.*, 63-77905, 1988
- 77 Campbell R E, Schmidt G F. Zirconium catalysts for syndiotactic polymers of vinylaromatic compounds. *US*, 4774301, 1988
- 78 Campbell R E, Hefner J G. Aluminoxane-titanocene catalysts for syndiotactic polymerization of styrene. *PCT Int. Appl. WO*, 88-10275, 1988
- 79 Schmidt G F, Campbell R E. Polymerization of vinylaromatic monomers by cyclopentadienylzirconium catalysts. *U. S. Pat. US*, 4408680, 1989
- 80 Tomotsu N, Maezawa H. Manufacture of syndiotactic styrene polymers and catalysts therefor. *Jpn. Pat.*, 01242607, 1989
- 81 Maezawa H, Tomotsu N and Kuramoto M. Process for producing styrene-based polymers and catalysts. *Eur. Pat. Appl. EP*, 322663, 1989
- 82 Maezawa H, Tomotsu N. Manufacture of syndiotactic styrene polymers and catalysts therefor. *Jpn. Pat.*, 01240503, 1989
- 83 Kuramoto M, Maezawa H and Hayashi H. Catalyst and process for producing styrenic polymer. *PCT Int. Appl. WO*, 8902901, 1989
- 84 Zambelli A, Oliva L and Pellicchia C. Soluble catalysts for syndiotactic polymerization of styrene. *Macromolecules*, 1989, 22(5): 2129~2130
- 85 Soga K. Polymerization catalysts for syndiotactic PS. *Jpn. Pat.*, 01210405, 1989
- 86 Soga K. Catalysts for preparation of syndiotactic styrene polymers. *Jpn. Pat.*, 0170510, 1989
- 87 Soga K, Nakatani H. Syndiotactic polymerization of styrene with supported Kaminsky-Sinn catalysts. *Macromolecules*, 1990, 23(4): 957~959
- 88 Soga K, Nakatani H. Polymerization of styrene with $\text{Mg}(\text{OH})_x\text{Cl}_{2-x}$ ($x=0\sim 2$)-supported $\text{Ti}(\text{OBu})_4$ catalysts combined with methylaluminoxane. *Macromolecules*,

- 1990, 23(5): 1558~1560
- 89 Imabayashi H, Ishikawa K, Yamamoto K and Itsumi T. Manufacture of syndiotactic styrene polymers. Jpn. Pat, 0291104, 1990
 - 90 Arai T, Tsuruta G and Tsuyama S. Manufacture of syndiotactic PS. Jpn. Pat, 02102206, 1990
 - 91 Tsuruta G, Arai T and Tsuyama S. Manufacture of stereoregular aromatic vinyl polymers with titanium - containing catalysts. Jpn. Pat, 02110106, 1990
 - 92 Imayoshi M, Maeda K and Seki J. Syndiotactic PS manufacture by vapor - phase polymerization. Jpn. Pat, 02238008, 1990
 - 93 Yamamoto K, Ishikawa K and Teshima H. Polymerization styrene catalyst of syndiotactic PS. Eur. Pat. Appl. EP, 390000, 1990
 - 94 Takeuchi M, Kuramoto M. Catalyst for polymerization of styrene. Eur. Pat. Appl. EP, 389981, 1990
 - 95 Tazaki T, Kuramoto M. Polymerization catalysts for preparation of styrene polymer. Jpn. Pat, 02252705, 1990
 - 96 Hirakawa K, et al. Manufacture of SPS with high crystallinity. Jpn. Pat, 02235911, 1990
 - 97 Chien W C J, Zdenek S. Syndiospecific polymerization of styrene: II. Monocyclopentadienyltributoxy titanium - methylaluminoxane catalyst. J. Polym. Sci., Part A: Polym. Chem., 1991, 29(9): 1253~1263
 - 98 Ishihara N, Marukomu R H G. Catalysts for syndiotactic polymerization of styrene. Jpn. Pat, 0359010, 1991
 - 99 Zambelli A, Pellecchia C, Oliva L, Longa P and Grassi A. Catalysts for SPS; a tentative interpretation of some experimental data. Makromol. Chem., 1991, 192(2): 223~231
 - 100 Sinn H, Kaminsky W. Adv. Oeganomet. Chem., 1980, 18(1): 99~102
 - 101 Chien W C J, Wang P B. Metallocene - methylaluminoxane catalysts for olefin polymerization: V. Comparison of Cp_2ZrCl_2 and CpZrCl_3 . J. Polym. Sci., Part A: Polym. Chem., 1990, 28(1): 15~38
 - 102 Chien W C J, Salajka Z. Syndiospecific polymerization of styrene: I. Tetrabenzyl titanium/methylaluminoxane catalyst. J. Polym. Sci., Part A: Polym. Chem., 1991, 29(9): 1243~1251
 - 103 Keii T, Doil Y and Soga K. Polymerization of propylene with $\text{Ti}(\text{O}i\text{Bu})_4/\text{MAO}/\text{SiO}_2$ catalyst. Makromol. Chem., 1984, 185(8): 1537~1557
 - 104 Grassie A, Longo P, Proto A and Zambelli A. Reactivity of some substituted styrene in the prosence of a syndiotactic specific polymerization catalyst. Macromolecules, 1989, 22(1): 104~108
 - 105 Zambelli A, Longo P, Pellecchia C and Grassi A. β -Hydrogen abstraction and regiospecific insertion in syndiotactic polymerization of styrene. Macromolecules, 1987, 20(8): 2035~2037

Synthesis of Stereoregular Styrene Polymers

Xu Guangxue, Lu Zejian, Lin Shangan

(Institute of Polymer Science, Zhongshan University, Guangzhou 510275)

Summary As a kind of functional materials of potential application, stereoregular styrene polymers have been widely studied. The review with 105 refs. (to July 1991) discussed synthetic methods, polymeric catalysts, polymerization mechanism, kinetics and development of stereoregular polystyrene.

Key words Isotactic polystyrene, Syndiotactic polystyrene, Styrene, Ziegler - Natta catalyst, Coordination polymerization