

Palladium-catalyzed arylation of ethylene. A synthetic route to styrenes, stilbenes, and poly(phenylene vinylene)s

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Abstract

Palladium-catalyzed arylation of ethylene (the Heck reaction) was studied using (chlorobenzene)Cr(CO)₃ complexes (I) and dibromobenzenes (II). At 100°C styrenes and divinylbenzenes were the major products and stilbenes, and oligo- and poly(phenylene vinylene)s were not formed in the range from 2 to 40 atm of ethylene pressure. At 140°C the polymeric products were formed in low yields. Two-step strategy, which includes coupling reactions of dihalobenzenes with ethylene and subsequently with divinylbenzenes, was successful in yielding poly(phenylene vinylene)s (PPVs). © 1999 Elsevier Science B.V. All rights reserved.

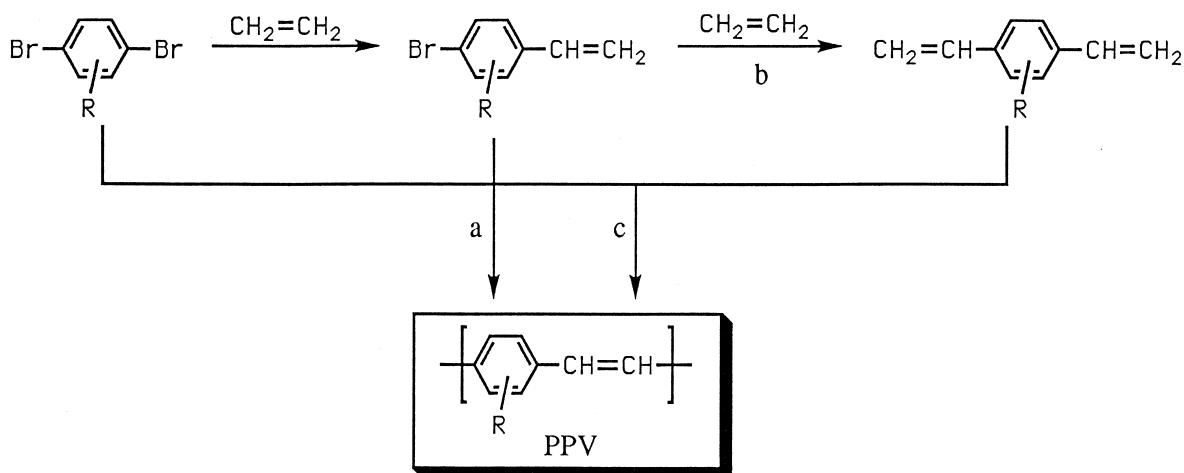
Keywords: Heck reaction; Styrene; Stilbene; Poly(phenylene vinylene)

1. Introduction

In recent years not only titanocenes or zirconocenes [1–3] but also Ni, Pd [4] and Fe, Co [5,6] compounds have found application to polymerization catalysts, which produce olefinic polymers with controlled properties. In general, late transition metal catalysts exhibit remarkable functional group tolerance or water-stability [7], compared to early transition metal catalysts.

Among the transition metals, palladium has been revealed to be versatile catalysts both in organic [8] and polymer synthesis [9–21]. The palladium-catalyzed C–C coupling reactions, which are widely applied to organic synthesis, have attracted interest of synthetic polymer chemists. For example, the Heck reaction is the coupling reaction of halobenzenes with olefins in the presence of bases [22]. A wide variety of halobenzenes and olefins with functional group can be used. Conjugated polymers have already been synthesized by the Heck reaction. Heitz [23] is one of the major contributors to this field. He and coworkers have applied the reaction to the synthesis of several substituted styrenes and PPVs, which have important electro-optical properties in materials technology [24]. Architectural approach by the Heck reaction to conjugated polymers has also been done [25]. Although there have been some advances in this strategy, these have been successful with a limited olefins and halobenzenes under limited conditions.

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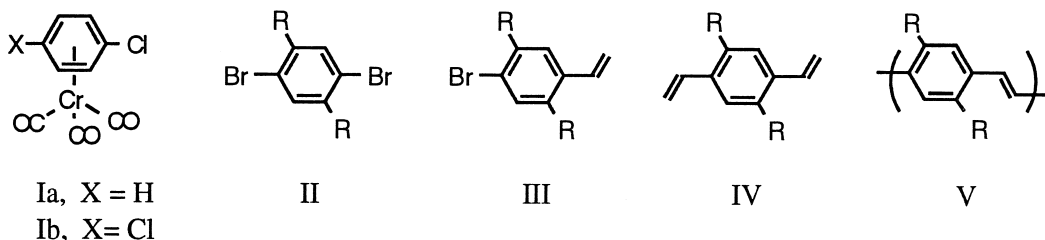


Scheme 1.

When dihalobenzenes are allowed to react with ethylene, the first reaction product is halostyrenes. There are two possibilities in the reactions of halostyrenes; the one is self-coupling to PPVs (a) and the other is further coupling with ethylene to afford divinylbenzenes (b). The latter gives finally PPVs (c) as shown in Scheme 1. The purpose of the present study is to obtain further details on the reaction of halobenzenes with ethylene under different conditions.

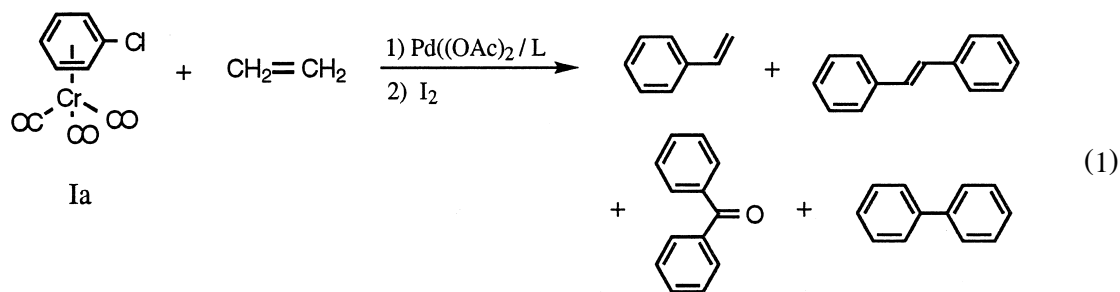
2. Results and discussion

Halobenzenes which were used in the present study are I and II. One limitation of the Heck reaction is that chlorobenzenes are usually unreactive [26]. The first step is the oxidative addition of halobenzenes to a palladium species. Introduction of a strong electron-withdrawing group into the phenyl ring promotes the oxidative addition [27]. Chromium tricarbonyl is similar to nitro group in terms of electron-withdrawing ability. In fact, Ia undergoes similar reactions to those bromo- or iodobenzene [28,29]. Initial test reaction was conducted as shown in Eq. (1) using Ia [30]. More detailed reactions were done in the present study. To simplify the analysis, the chromium complexes formed were oxidized with iodine and the



- a, R = n-C₆H₁₃
 b, R = OCH₃
 c, R = O(CH₂)₇CH₃
 d, R = O(CH₂)₃SO₃Na

resulting Cr-free products were analyzed by gas chromatography. The results are summarized in Table 1. If the reaction was carried out at 2 atm of ethylene, styrene as well as stilbene were



formed in moderate yields. Under high pressure of ethylene the oxidative addition of halobenzene to the Pd catalyst, which is the first step of the arylation of ethylene, is hindered by strong coordination of ethylene. Therefore, even at 1.4 atm (20 psi) the usual Heck reaction of ethylene takes place smoothly [31]. In the present system, however, side reactions occurred at 2 atm with formation of benzophenone and biphenyl. The yield of the target products were rather low than those of the by-products. Caldirola et al. [32] have reported the transfer of CO from (η^6 -arene)Cr(CO)₃ complexes in Stille-type palladium-catalyzed cross-coupling reaction of the coordinated arene. It is to note that Cr(CO)₃ moiety serves as a source of CO in the ‘self-coupling’ of coordinated chlorobenzene leading to benzophenone.

For comparison, styrene (5 equivalents) was subjected to the coupling with Ia (Table 1). Stilbene was the major product. 1,1-Diphenylethylene was formed in a low yield. It is likely that the formation of benzophenone and biphenyl was unavoidable in the reaction of this type. The reaction of Ib with ethylene gave chlorostyrene and divinylbenzene in low yields (Table 2). In this reaction the formation of chlorobenzophene was confirmed by IR spectra.

The coupling products (IIIa and IVa) of IIa with ethylene were easily analyzed by gas chromatography. The results are shown in Table 3. Bromostyrene [IIIa] and divinylbenzene (IVa) were formed in comparable yields for 4 h. Prolonged reaction resulted in increase of the yield of IVa. Increasing

Table 1
Reaction of (C₆H₅Cl)Cr(CO)₃ with ethylene and styrene by Pd(OAc)₂/L at 100°C for 6 h

Olefin () ^a	L	Solvent	Product yield (%)			
			Styrene	Stilbene () ^b	Benzophenone	Biphenyl
Ethylene (2)	PPh ₃	Toluene	22	9	17	17
Ethylene (2)	Ph ₂ P(CH ₂) ₂ PPh ₂	Toluene	40	5	10	4
Ethylene (40)	Ph ₂ P(CH ₂) ₃ PPh ₂	Toluene	56	–	–	–
Styrene	–	Toluene		22 (3)	1	1
Styrene	PPh ₃	Toluene		58 (2)	11	8
Styrene	Ph ₂ P(CH ₂) ₂ PPh ₂	Toluene		60 (4)	8	3
Styrene	Ph ₂ P(CH ₂) ₃ PPh ₂	Toluene		54 (2)	24	15
Styrene	PPh ₃	Acetonitrile		42 (2)	14	15
Styrene	P(<i>o</i> -tolyl) ₃	Acetonitrile		56 (2)	24	4

^aPressure of ethylene (atm).

^bYield of 1,1-diphenylethylene (%) (C₆H₅Cl)Cr(CO)₃, 0.6 mmol; Styrene, 3.0 mmol; Pd(OAc)₂, 0.03 mmol; L, P/Pd = 2; Solvent, 5 ml, Et₃N, 1.0 mmol.

Table 2
Reaction of (*p*-C₆H₄Cl₂)Cr(CO)₃ with ethylene

Ethylene (atm)	Ligand (mmol)	Product yield (%)	
		Chlorostyrene	Divinylbenzene
2	P(<i>o</i> -tolyl) ₃ (0.06)	13	0
40	P(<i>o</i> -tolyl) ₃ (0.06)	29	10
2	Ph ₂ P(CH ₂) ₂ PPh ₃ (0.03)	7	0

(*p*-C₆H₄Cl₂)Cr(CO)₃, 0.6 mmol; Pd(OAc)₂, 0.03 mmol; CH₃CN, 5 ml; Et₃N, 1.5 mmol; 100°C, 16 h.

ethylene pressure decreased the yields of both IIIa and IVa. In all reaction shown in Table 3, dibromobenzene, which remained unchanged, was detected. At 140°C, a small amount of methanol-insoluble yellow solid was isolated (shown as 'Others' in Table). The IR spectrum has medium bands at 960, 910 and 990 cm⁻¹, which correlate to trans C=C bond and vinyl group. These observation means the presence of molecules with two bromo-, two vinyl-, and bromovinyl end groups. Variables of ethylene, which influence on the product distribution, are pressure and total amount of ethylene. In the present study 0.6 mmol of halobenzenes was used in a 50 ml stainless steel autoclave. Therefore, a large excess amount of ethylene was present even at 2 atm. As bromostyrene (IIIa) and divinylbenzene (IVa) were formed on one side and dibromobenzene (IIa) remained unchanged on the other, the reaction of ethylene of this type is not selective so long as dibromobenzenes are used.

Alkoxy-substituted dibromobenzenes (IIb, c) underwent the reaction similarly and the expected products were obtained in moderate yields (Table 4). In this reaction, however, the products were not analyzed by gas chromatography due to their high boiling points. The profile of the reaction was expressed by 'vinylation', which was determined by comparing the ¹H NMR peak area of the vinyl group with that of the OCH₃ or OCH₂ group. Thus, 50% vinylation means that half of Br was substituted by vinyl group in average. Though the ratio of III to IV was not determined, both III and IV were presumed to be formed by analogy to the reaction of IIa. At 140°C, an insoluble solid was separated from the solution.

Since the sulfonate functionality of IId serves as the charge-compensate dopant ion [33], IId constitutes an interesting building-block in conjugated polymers. The reaction of water-soluble IId was conducted under aqueous conditions using sodium hydrogen carbonate as base [34]. At 2 atm, which is favorable pressure of ethylene under organic conditions, the reaction did not take place presumably due to the low solubility of ethylene into the mixed solvent of water and acetonitrile. At higher pressure (20–30 atm), the reaction occurred. Unlike the reaction in organic media, palladium was recovered as a black precipitate. All reactions were conducted using in situ addition of the ligand

Table 3
Reaction of dibromobenzene (IIa) with ethylene

Ethylene (atm)	Time (h)	Temp. (°C)	Product yield (%)		
			Bromostyrene (IIIa)	Divinylbenzene (IVa)	Others ^a
2	4	100	31	39	
2	16	100	17	56	
2	16	140	11	57	~ 10
10	16	100	34	34	
40	16	100	23	3	

^aMethanol-insoluble solid, IR 910, 990(s), 965(m). The reaction conditions were carried out such as has been described in Table 2.

Table 4
Reaction of dibromobenzenes (IIb, c and d) with ethylene

R of II	Ethylene (atm)	Ligand	Solvent	Base	Temp. (°C)	Time (h)	Vinylation ^a (%)	Others ^b (%)
OCH ₃	2	P(<i>o</i> -tolyl) ₃	CH ₃ CN	Et ₃ N	100	16	60	
OCH ₃	7	P(<i>o</i> -tolyl) ₃	CH ₃ CN	Et ₃ N	100	16	14	
OCH ₃	2	P(<i>o</i> -tolyl) ₃	CH ₃ CN	Et ₃ N	100	70	70	
OCH ₃	2	P(<i>o</i> -tolyl) ₃	CH ₃ CN	Et ₃ N	140	16	41	ca.30
O(CH ₂) ₇ -CH ₃	2	P(<i>o</i> -tolyl) ₃	CH ₃ CN	Et ₃ N	100	16	46	
O(CH ₂) ₇ -CH ₃	2	P(<i>o</i> -tolyl) ₃	CH ₃ CN	Et ₃ N	140	16	92	ca.30
O(CH ₂) ₃ SO ₃ Na	2	PPh ₃	CH ₃ CN/H ₂ O	NaHCO ₃	100	70	~ 0	
O(CH ₂) ₃ SO ₃ Na	20	PPh ₃	CH ₃ CN/H ₂ O	NaHCO ₃	100	70	54	
O(CH ₂) ₃ SO ₃ Na	30	P(<i>o</i> -tolyl) ₃	CH ₃ CN/H ₂ O	NaHCO ₃	100	16	55	
O(CH ₂) ₃ SO ₃ Na	30	PPh ₃	CH ₃ CN/H ₂ O	NaHCO ₃	100	16	36	
O(CH ₂) ₃ SO ₃ Na	40	PPh ₃	CH ₃ CN/H ₂ O	NaHCO ₃	100	70	43	
O(CH ₂) ₃ SO ₃ Na	50	PPh ₃	CH ₃ CN/H ₂ O	NaHCO ₃	100	70	40	
O(CH ₂) ₃ SO ₃ Na	30	dppm ^c	CH ₃ CN/H ₂ O	NaHCO ₃	100	70	16	

^aSoluble part.

^bMethanol-insoluble.

^c(C₆H₅)₂P(*m*-C₆H₄SO₃Na) II, 0.6 mmol; Pd(OAc)₂, 0.03 mmol; Base, 1.5 mmol; CH₃CN, 5 ml; CH₃CN/H₂O 5 ml/5 ml.

to Pd(OAc)₂. Instability of the catalyst in the aqueous system may be ascribed to decomposition of ligandless Pd to Pd(0), while the catalyst in the organic system is stabilized by ligand or a large amount of Et₃N, which is present as base. After adding ether and water, the aqueous layer was separated from the organic phase, which contained catalyst, and then the products were isolated by evaporating water under reduced pressure, followed by washing with ether. The vinylation was determined by measuring ¹H NMR in D₂O. The vinylation was low in general; it was at the highest ca. 50%. Use of water-soluble phosphine (dppm, diphenylphosphino monosulfonate, (C₆H₅)₂P(*m*-C₆H₄SO₃Na)) brought about decrease of the yield. Compared with the reaction in organic media, the reaction of IIId under aqueous conditions is slow to some extent, thus requires longer time.

In summarizing the present arylation of ethylene, the reaction at 100°C gives both styrenes and divinylbenzenes. Further coupling products such as stilbenes or poly(phenylene vinylene)s (PPVs) are difficult to be obtained. Around 140°C, the latter are formed in low yields. As described above, it is difficult to obtain PPVs in 'one-pot' from the reaction of dihalobenzenes with ethylene, even if ethylene is charged in a 1:1 molar ratio.

Consequently, it is our feeling that a possible route to target stilbenes or PPVs by the Heck reaction requires two-stage coupling reaction of dihalobenzenes; the first is with ethylene to form divinylbenzenes and the second is with the divinylbenzenes. In fact, coupling of dihalobenzenes with divinyl-

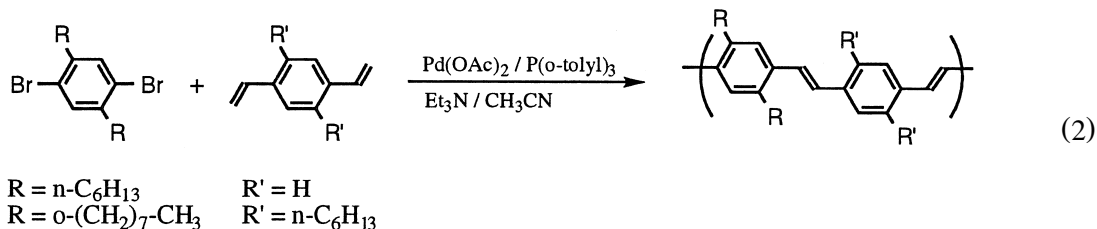
Table 5
Coupling of dibromobenzenes (II) with divinylbenzenes (IV) to poly(phenylene vinylene)s at 100°C for 70 h

R		Yield (%)	Mol. wt.
II	IV	V	Mn/10 ³
<i>n</i> -C ₆ H ₁₃	H	70	2.5
<i>o</i> -(CH ₂) ₇ -CH ₃	H	82	1.5
<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	85	12.0 ^a

^aλ_{max} (in CHCl₃), 389 nm.

II = IV, 0.6 mmol; Pd(OAc)₂, 0.03 mmol; P(*o*-tolyl)₃, 0.06 mol; Et₃N, 1.5 mmol; CH₃CN, 5 ml.

benzenes proceeded readily and PPVs were formed in high yields (Eq. (2). Table 5). In this case, however, polymers separated gradually from the solution with reaction time. Both monomers (IIa and IVa) having the *n*-hexyl substituent gave a yellow, high



molecular weight polymer, which showed brilliant green fluorescence.

3. Experimental

All operations were performed under an atmosphere of argon. Organic solvents were purified by the conventional methods and stored under argon. Distilled water was degassed with argon before use. Chromium complexes (I) [35], dibromobenzenes IIa [36], IIb,c,d [32] were prepared by the reported methods. ¹H NMR spectra were recorded on a JEOL JNM-GX270 spectrometer. GC and GPC were performed on Shimadzu GC-4C (column, Silicon DC 560, 2 m) and on Shimadzu RID-6A and LC-6A (column, Asahipak GS-510, 7.6 mm i.d.), respectively.

3.1. Reaction of I with ethylene

In a 50 ml stainless steel autoclave were placed a magnetic stirrer, I (0.6 mmol), Pd(OAc)₂ (0.03 mmol), phosphine (0.06 or 0.03 mmol, P/Pd = 2), and biphenyl as an internal standard. The system was placed under ethylene. After adding acetonitrile (5 ml) and Et₃N (1.0 or 1.5 mmol), ethylene was charged up and the autoclave was heated. The reaction conditions are shown in Tables 1 and 2. After reaction, ether (20 ml) and iodine (ca. 0.7 mmol) were added and the mixture was stirred overnight at room temperature. The solution was washed with aqueous sodium hydrogensulfite (0.2 g) in water (20 ml) dried over CaCl₂, and evaporated. The resulting residue was analyzed by GC at programmed temperature from 170 to 250°C.

3.2. Reaction of I with styrene

The reaction was performed in the autoclave similarly as described above, using styrene instead of ethylene (Table 1).

3.3. Reaction of IIa

The reaction was performed similarly as described in the reaction of I with ethylene. After the reaction, the solution was filtered, washed with water and dried over CaCl₂. After evaporating solvent, the products were analyzed by GC (Table 3).

3.4. Reaction of *Ib,c*

The reactions were conducted similarly as those of *IIa*. The products were analyzed by ^1H NMR (in CDCl_3) (Table 4).

3.5. Reaction of *IId*

The reaction was conducted in CH_3CN (5 ml) and degassed H_2O (5 ml) in the presence of NaHCO_3 (0.13 g). After adding ether and water, the aqueous solution was evaporated to dryness and the resulting solid was washed with ether, followed by NMR analysis (in D_2O) (Table 4).

3.6. Reaction of *II* with *IV* (polymerization)

In a 50 ml flask were placed a magnetic stirrer, *II* (0.6 mmol) and divinylbenzene *IV* (0.6 mmol), $\text{Pd}(\text{OAc})_2$ (0.03 mmol) and tri-*o*-tolylphosphine (0.06 mmol). The flask was placed under argon. Acetonitrile (5 ml) and Et_3N (1.5 mmol) were added and the flask was heated at 100°C for 20 h with stirring. Methanol (50 ml) was added to the solution. Precipitated polymer was filtered, washed with methanol, and dried under reduced pressure (Table 5).

References

- [1] H. Sinn, W. Kaminsky, H.J. Wollmer, R. Woldt, *Angew. Chem. Int. Ed. Engl.* 19 (1980) 390.
- [2] H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [3] A.A. Montagna, R.M. Burkhart, A.H. Dekmezian, *CHEMTECH*, Dec. 1997, p. 26.
- [4] I.K. Johnson, M.C. Killian, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414.
- [5] B.L. Small, M. Brookhart, A.M.A. Bennett, *J. Am. Chem. Soc.* 120 (1998) 4049.
- [6] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Uddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, *Chem. Commun.*, 1998, p. 849.
- [7] D.M. Lynn, S. Kanaoka, R.H. Grubbs, *J. Am. Chem. Soc.* 118 (1996) 784.
- [8] J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, Chichester, 1995.
- [9] M. Bockmann, K. Kelly, *Chem. Commun.*, 1989, p. 532.
- [10] Y. Ito, E. Ihara, M. Murakami, M. Shiro, *J. Am. Chem. Soc.* 112 (1990) 6446.
- [11] Y. Imai, *CHEMTECH* 21 (1991) 560.
- [12] T.I. Wallow, B.M. Novak, *J. Am. Chem. Soc.* 113 (1991) 7411.
- [13] R. Giesa, M. Klapper, R.C. Schulz, *Makromol. Chem. Macromol. Symp.* 44 (1991) 1.
- [14] M. Suzuki, *J. Synth. Org. Chem. Jpn.* 51 (1993) 141.
- [15] A. Sen, *Acc. Chem. Res.* 26 (1993) 303.
- [16] E. Dent, P.H.M. Budzelaan, *Chem. Rev.* 96 (1996) 663.
- [17] P. Corradini, C. DeRosa, A. Pannunzi, G. Petrucci, P. Pino, *Chimia* 44 (1990) 52.
- [18] M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U.W. Suter, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 989.
- [19] M. Brookhart, M.I. Wagner, *J. Am. Chem. Soc.* 116 (1994) 3641.
- [20] K. Nozaki, N. Sato, Y. Tomomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara, N. Koga, *J. Am. Chem. Soc.* 119 (1997) 12779.
- [21] A.L. Safir, B.M. Novak, *J. Am. Chem. Soc.* 120 (1998) 643.
- [22] R.H. Heck, *Organic reactions*, Vol. 27, Robert E. Krieger Publishing, FL, 1989, p. 345.
- [23] W. Heitz, *Angew. Makromol. Chem.* 223 (1994) 135, and references cited therein.
- [24] H. Meier, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1399.
- [25] T. Maddux, W. Li, L. Yu, *J. Am. Chem. Soc.* 119 (1997) 844.
- [26] Y.B.-David, M. Portnoy, M. Gozin, D. Milstein, *Organometallics* 11 (1992) 1995.
- [27] V. Dufaud, J.T. Cazat, J.M. Basset, M. Mathieu, J. Jaud, J. Wassermann, *Organometallics* 10 (1991) 4005.
- [28] R. Mutin, C. Lucas, J.T. Cazat, V. Dufaud, *Chem. Commun.*, 1988, p. 896.
- [29] W.J. Scott, *Chem. Commun.*, 1987, p. 1755.

- [30] J. Kiji, *Macromol. Symp.* 105 (1996) 167.
- [31] J.E. Plevyak, R.F. Heck, *J. Org. Chem.* 43 (1978) 2454.
- [32] P. Caldirola, R. Chowdhury, A.M. Johansson, V. Hacksell, *Organometallics* 14 (1995) 3897.
- [33] A.D. Child, J.R. Reynolds, *Macromolecules* 27 (1994) 1975.
- [34] J. Kiji, T. Okano, T. Hasegawa, *J. Mol. Catal. A: Chem.* 97 (1995) 73.
- [35] V. Percec, S. Okita, *J. Polym. Sci. A: Polym. Chem.* 31 (1993) 923.
- [36] M. Rehahn, A.-D. Schlutter, G. Wegner, W.J. Feast, *Polymer* 30 (1989) 1054.