DOI: 10.1002/chem.200800558

Stannylated Polynorbornenes as New Reagents for a Clean Stille Reaction

Nora Carrera, Enrique Gutiérrez, Rut Benavente, M. Mar Villavieja,
Ana C. Albéniz,* and Pablo Espinet*[a]

Abstract: New functionalized polynorbornenes have been obtained in good yields by vinylic copolymerization of norbornene with a (norbornenyl)Sn-Bu_2Cl monomer, catalyzed by [Ni-$(C_6F_5)_2(SbPh_3)_2$]. Subsequent functionalization produces a wide variety of polymers with different $-SnBu_2R$ groups (R = aryl, vinyl, alkynyl). The polymers can be used as R-transfer reagents in Stille couplings, thereby providing easy workup and separation of the polymeric tin byproducts from the coupling products. Tin contents of around 0.05 wt % are found in the Stille products. The stannylated polymers can be recycled and reused with good efficiency.

Keywords: C−C coupling · green chemistry · polymers · recycling · tin

Introduction

The Stille reaction is one of the most powerful tools in C−C coupling processes [Eq. (1)].[1,2] Compared with other main group derivatives, organotin reagents offer many advantages: air stability, resistance to hydrolysis, easy handling and storage, and tolerance to a wide variety of functional groups. These properties make the reaction versatile and wide ranged. Furthermore, the Stille coupling is usually carried out under mild conditions and does not require the use of additives such as bases. These features make the reaction very useful in general organic synthesis,[2] polymer functionalization,[3] and particularly in natural product syntheses, in which C−C couplings have to be accomplished preserving other, often reactive, functional groups present in the molecule.[4] The mechanistic aspects of the reaction have been studied in detail and a fair understanding of the process has been reached.[5]

$$R^1X + SnR_3R^2 \xrightarrow{[Pd]} R^1{-}R^2 + SnR_3X \qquad (1)$$

An important drawback in the industrial use of the reaction is the formation of toxic tin byproducts SnR_3X, which are harmful residues difficult to separate from the target product. Even at the laboratory scale, the separation of tin byproducts is very cumbersome. Many efforts have been made to address this problem. Thus, tin reagents modified with polyaromatic rings improve the separation of the byproducts by adsorption on activated carbon.[6] Tin derivatives with fluorinated alkyl substituents can be separated by extraction in fluorocarbon solvents.[7] In Ni-catalyzed Stille reactions, monoorganotin reagents $SnRCl_3$ are an alternative to the common tetraorganotin reagents: although they do not bring special advantages in the separation process, the byproducts formed are less toxic.[8] Maleczka et al. introduced the use of tin derivatives in catalytic amounts in Stille couplings.[9] The process is based on the in situ hydrostannylation of alkynes that leads to vinylic tin derivatives, which limits the range of application to vinylation reactions.

An approach that addresses simultaneously the problem of separation of the tin residues and their recycling is the use of a polymeric matrix containing the tin functionality. The use of a tin-containing polymeric matrix has met with success in other organic reactions such as free radical processes,[10] transesterification reactions,[11] allylation of aldehydes,[12] halogenation of aromatic amines,[13] lactonization,[14] and other reactions,[15] but only a few attempts have been made to use polymeric tin reagents in the Stille reaction[16] or in the catalytic tin Stille vinylation mentioned above[17] The polymers used in all these reactions are polystyrene resins, most of them synthesized by functionalization of preformed polymer supports. In the case of the Stille re-

---

[a] N. Carrera, E. Gutiérrez, R. Benavente, M. M. Villavieja,
Prof. A. C. Albéniz, Prof. P. Espinet
IU CINQUIMA/Química Inorgánica
Universidad de Valladolid
47071-Valladolid (Spain)
Fax: (+34) 983-423013
E-mail: albeniz@qi.uva.es
espinet@qi.uva.es

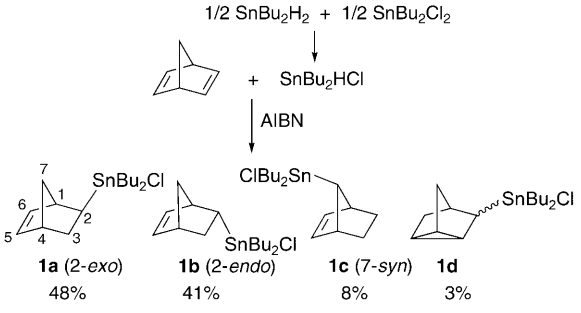
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200800558.

action, easy separations were reported and some authors commented on the possibility of reusing the polymers, but no data of recyclability of the polymeric reagents were given.

Considering the scant precedents, we planned to prepare a different kind of stannylated polymer tailored for its use in the Stille reaction. It should have a polymeric aliphatic skeleton and a polymer–Sn link resistant to transmetalation so that the other organic groups on Sn will be selectively transmetalated while the tin residue remains on the polymer. The structural frame chosen in this work was a polynorbornene skeleton. We report here on the synthesis of copolymers of norbornene and chlorostannylated norbornenes, and their application as efficient and reusable reagents in the Stille reaction. Although our main goal is the use of the stannylated polymers in the Stille reaction, it is worth noting that tin polymers have found use in other applications (antifouling paints, precursors of tin-containing films, etc.),[18] which widens their interest.

Results and Discussion

Synthesis of chlorostannylated norbornene: The stannylated norbornene used in this work, (norbornenyl)$SnBu_2Cl$ (**1**), is not commercially available. It was prepared by radical hydrostannylation of norbornadiene using $SnBu_2HCl$.[19] The radical addition of the closely related $SnMe_3H$ has been used before in the preparation of trimethylstannyl norbornene derivatives, and was shown to afford a mixture of four isomers.[20,21] Similarly, we observed a mixture of four isomers upon addition of $SnBu_2HCl$ in the ratio shown in Scheme 1. The 2-*exo* (**a**), 2-*endo* (**b**), and 7-*syn* (**c**) isomers were assigned by using the ^1H NMR spectroscopy olefinic signals and the $^3J_{Sn,C}$ values in the ^{13}C NMR spectra for the *exo* (**a**) and *endo* (**b**) isomers (see the Experimental Section).[22] The $^{119}Sn\{^1H\}$ NMR spectrum clearly shows four signals corresponding to the four isomers **a**–**d**. Derivatization of **1a**–**d** to (norbornenyl)$SnBu_2(C_6H_4OMe)$ (**2a**–**d**) by treatment with $MgBr(C_6H_4OMe)$ was also carried out to aid with the characterization of the isomeric mixture. The ratio of isomers **1a**–**d** was kept in the new derivatives **2a**–**d** (see the Supporting Information).

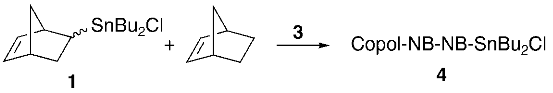


Scheme 1. Synthesis of the stannylated monomer **1** (as a mixture of isomers).

These isomers could not be separated by conventional preparative methods, so the mixture was used for the subsequent reactions. For the sake of brevity, we will refer to these mixtures **1a**–**d** as **1**, and it should be assumed that structural mixtures are also present in the polymers derived from **1**.

Copolymerization reactions: The chlorostannylated polymers were synthesized by vinylic copolymerization of chlorostannylated norbornene derivatives. Many transition-metal catalysts are able to efficiently polymerize norbornene (NB) by an insertion mechanism,[23] but fewer systems are active in the vinylic polymerization of norbornene derivatives.[24,25,26] In fact, there is no precedent for the vinylic polymerization of stannylated norbornenes. Complex $[Ni(C_6F_5)_2(SbPh_3)_2]$ (**3**) was chosen as catalyst because it has been reported to be fairly active and easy to handle.[26]

Complex **3** was not effective in the homopolymerization of **1**, but the copolymerization of **1** and NB (ratios 1:1, 1:2, 1:5) afforded copolymers, as white solids, in fairly good yields [Eq. (2)]. The absence of resonances in the olefinic region of the ^1H NMR spectra of the polymers supports a vinylic polymerization mechanism. The polymers show pentafluorophenyl end groups (the ^{19}F NMR spectroscopy chemical shifts in the F_{ortho} region are characteristic of C_6F_5 groups bound to carbon),[27] which suggest an insertion mechanism of polymerization initiated by insertion of NB or **1** into the $Ni{-}C_6F_5$ bond.[24e,26] Since **1** is a mixture of isomers (**1a**–**d**), a complicated polymer morphology can be anticipated. Moreover, a complex stereochemistry and even connectivity in the polymers obtained by vinylic polymerization of norbornene has been reported.[28–30] In other words, the polymers cannot be expected to possess a regular structure. Accordingly, the $^{119}Sn\{^1H\}$ spectra display one broad signal with a characteristic trialkyltin chloride chemical shift value ($\delta =$ 144 ppm). Broad signals are also observed in the $^{13}C\{^1H\}$ NMR spectra for the NB skeleton, in which the absence of signals around $\delta = 20$ ppm point to an *exo* norbornene enchained polymer.[29,31]



(2)

Table 1 shows the results obtained for different monomer feed ratios. Although the ^1H NMR spectroscopy signals arising from NB and **1** appear overlapped, the incorporation of **1** was easily determined by quantitative determination of the chloro content in the copolymers.[32] Table 1 shows that the final NB/**1** ratio does not reproduce the monomer feed ratio. The percentage of NB is larger in the copolymer (by a factor of about two) and increases with the NB content in the feed. Yields also increase for higher starting NB/**1** ratios. The polymers obtained are highly polydisperse ($M_w/M_n = 4$–6), with molecular weights in the range from 4×10^4 to 8×10^4.

Table 1. Results for the copolymerization reactions of **1** and norbornene (NB).[a]

Entry	NB/**1**/[Ni] [mol]	Yield [%][b]	Monomer ratio NB/**1** in copolymer [mol][c]
1	50/50/1	66	2.8/1
2	100/50/1	78	4.4/1
3	250/50/1	85	6.1/1

[a] The reactions were carried out at room temperature in CH_2Cl_2 (4 mL), from **1** (0.67 g) and the corresponding amount of a 2.52 M solution of NB in CH_2Cl_2. [b] Yields are based on the total mass of monomers in the feed. [c] Determined by analysis of the chloro content in the copolymer.

The different isomers (**1a–d**) in **1** are not equally active in the copolymerization reaction. Their activity can be assessed from their ratio in the starting mixture of monomers and in the unreacted residue after quenching a copolymerization reaction and precipitating the polymer. Figure 1 shows the ^1H and ^{119}Sn NMR spectra in the olefinic region for both samples. It is clear that the 2-*exo* isomer **1a** polymerizes the fastest, and the approximate polymerization rates decrease in the order **1a** (2-*exo*) > **1b** (2-*endo*) > **1c** (7-*syn*).

Synthesis of organostannylated copolymers: Experiments showed that catalyst **3** is equally active in the copolymerization of norbornene with organostannylated monomers (norbornenyl)SnR_2R^2. However, a more convenient method is to use chlorostannylated NB/**1** copolymers (copol-NB-NBSnBu$_2$Cl, **4**) as a general precursor for polymers with new Sn–R bonds, by substitution of the Sn–Cl bond [Eq. (3)]. This method avoids the need to synthesize and copolymerize each monomer (norbornenyl)$SnBu_2R^2$ from scratch to produce each copol-NB-NBSnBu$_2$R^2 polymer. A NB/**1** = 1:1 ratio in the monomer feed (as in entry 1, Table 1) was chosen for large-scale synthesis of **4** (about 20 g), which was obtained as a white solid after precipitation in methanol, in which the residual monomers are soluble. This afforded a polymer with a good incorporation of monomer **1** (see Table 1), which was used for the syntheses of **5–9** and led to the organostannylated copolymers in good yields (70–80%).

$$\underset{\mathbf{4}}{\text{Copol-NB-NB-SnBu}_2\text{Cl}} \xrightarrow{\text{MR}^2} \underset{\mathbf{5\text{-}9}}{\text{Copol-NB-NB-SnBu}_2\text{R}^2} \qquad (3)$$

M = MgBr, R^2 = CH=CH$_2$ (**5**)

M = Li, R^2 = C_6H_4OMe-*p* (**6**); C_6H_4F-*p* (**7**); $C_6H_4CF_3$-*p* (**8**); C≡CPh (**9**)

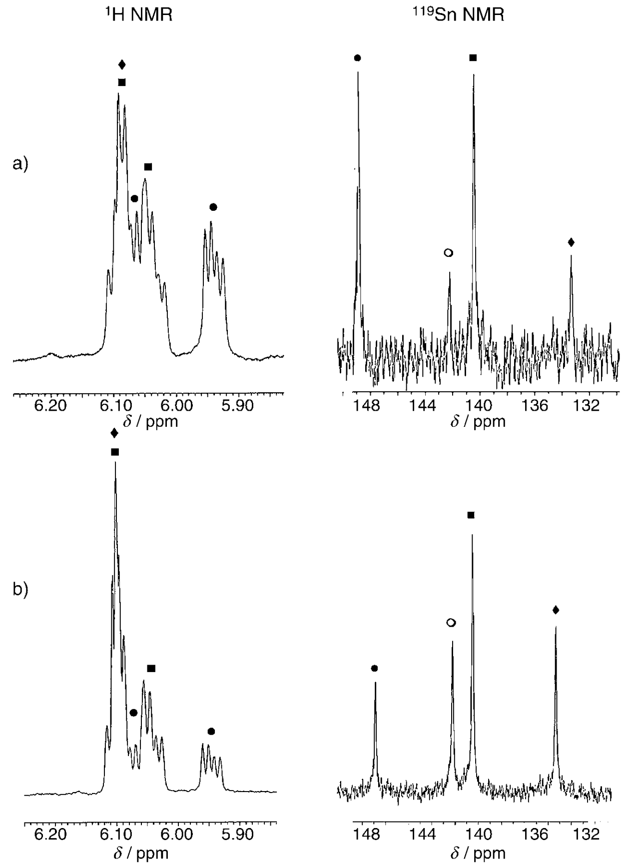


Figure 1. ^1H (olefinic region) and ^{119}Sn NMR spectra of **1** (● = **1a**, ■ = **1b**, ◆ = **1c**, ○ = **1d**): a) starting reagent; b) unreacted residue after quenching a copolymerization with NB.

Stannylated polymers as reagents in Stille reactions: The organostannylated polymers **5–9** were used as reagents in the Stille reaction [Eq. (4)]. A screening for applicability in the reaction was performed. A few hydrocarbyl halides with different oxidative addition rates to palladium were chosen, including a fluorinated aryl that allows an easy reaction follow up by using ^{19}F NMR spectroscopy. $[\{Pd(AsPh_3)(\mu\text{-}Br)(C_6F_5)\}_2]$ was used in most cases since it is a stable complex, easy to store and handle, and thus convenient for use as catalyst in Stille couplings. However, the common allylic complex $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ can also be used, as demonstrated in entry 5, Table 2. The results for a number of electrophiles and nucleophiles are collected in Table 2.

The content of Sn–R^2 groups in the polymers was determined by using ^1H NMR spectroscopy using an internal standard (see the Supporting Information), so equimolar amounts of the electrophile and Sn–R^2 could be used. The conditions selected (solvent and temperature) were chosen to favor a fast oxidative addition of the organic halide. Benzoquinone was added to the reactions involving allylic derivatives (entries 4–7, Table 2) to favor the reductive elimination step.[33] The results in Table 2 show that these polymers can be used efficiently in a variety of couplings, and polymer **4** makes an excellent and general precursor of tin–polymer reagents for the Stille reaction. Usually the reactions are noticeably slower than using monomeric tin derivatives, proba-

$$R^1X + \underset{\mathbf{5\text{-}9}}{\text{Copol-NB-NBSnBu}_2\text{R}^2} \xrightarrow{[\text{Pd}]} \underset{\mathbf{10\text{-}18}}{R^1\text{-}R^2} + \text{Copol-NB-NBSnBu}_2\text{X} \qquad (4)$$

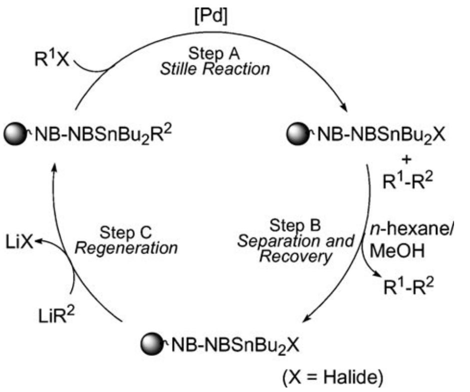
Table 2. Stille reactions using copol-NB-NBSnBu$_2$R^2 **5–9** as reagents.

Entry	R^{1}X	Polymer, R^2	Solvent	T [°C]	Time	R^1–R^2 [%]
1[a]	C_6F_5I	**5**, $CH_2{=}CH$	dioxane	90	1 day	**10** (67)
2[a]	C_6F_5I	**6**, p-OMe$-C_6H_4$	dioxane	90	3 days	**11** (72)
3[a]	p-$NO_2-C_6H_4I$	**9**, $PhC{\equiv}C$	$CDCl_3$	50	1 day	**12** (100)
4[a,b]	$CH_2{=}CH-CH_2Cl$	**6**, p-OMe$-C_6H_4$	$CDCl_3$	50	8 h	**13** (93)
5[c]	$CH_2{=}CH-CH_2Cl$	**6**, p-OMe$-C_6H_4$	$CDCl_3$	50	1 day	**13** (90)
6[a,b]	$CH_2{=}CH-CH_2Cl$	**7**, p-F$-C_6H_4$	$CDCl_3$	50	2 days	**14** (100)
7[a,b]	$CH_2{=}CH-CH_2Cl$	**8**, p-$CF_3-C_6H_4$	$CDCl_3$	50	1 day	**15** (100)
8[a]	PhCOCl	**6**, p-OMe$-C_6H_4$	$CDCl_3$	50	18 h	**16** (66)
9[a]	PhCOCl	**7**, p-F$-C_6H_4$	$CDCl_3$	50	18 h	**17** (64)
10[a]	PhCOCl	**9**, $PhC{\equiv}C$	$CDCl_3$	50	18 h	**18** (81)

[a] [{Pd(AsPh$_3$)(μ-Br)(C$_6$F$_5$)}$_2$] (2.5 % mol) was used as catalyst. [b] Benzoquinone (2.5 % mol) was added (see text and ref. [33]). [c] [{Pd(η^3-C$_3$H$_5$)(μ-Cl)}$_2$] (0.5 % mol) was used as catalyst and benzoquinone (1 % mol) was added.

bly reflecting higher hindrance of the reactive tin centers in the polymers (e.g., in entry 2, polymer **6** produces 72 % of the bisaryl $C_6F_5-C_6H_4OMe$ (**11**) in 3 days, whereas SnBu$_3$(C$_6$H$_4$–OMe-p) under the same reaction conditions produces 100 % yield after only 6 h). However, in some cases, such as the reactions to give *para*-methoxy allyl benzene (**13**) (entries 4 and 5, Table 2), polymer **6** is about as fast as SnBu$_3$(C$_6$H$_4$–OMe-p).

Polymer recovery and recycling: To check the feasibility of using these polymers in the Stille reaction, as far as easy workup, recovery, and recycling are concerned, two model reactions were chosen that correspond to entries 2, 5, and 6 in Table 2. Scheme 2 shows the reactions carried out in each cycle for the synthesis of the coupling product and the recovery of the tin organopolymer.



Scheme 2. Cycle of recycling of stannylated polynorbornenes in a Stille reaction.

Recycling of reaction in entry 5 (Table 2): The starting polymer **6** [produced from a copolymer **4** with a NB/**1** = 2.9:1 molar ratio as shown in Equation (3)] was a white solid that is soluble in chloroform and THF to give viscous solutions, but insoluble in MeOH or *n*-hexane. It can be used and recycled at least five times (Table 3; see the Experimental Section for details). This protocol was repeated twice independently, each series of experiments including five cycles of reuse, with similar results.

The Stille reactions were carried out using a molar ratio allyl chloride/Sn-C$_6$H$_4$-OMe-p = 1:1 and just 0.5 % mol of palladium catalyst, at 50 °C. In every cycle, before running the next Stille reaction, the Sn-C$_6$H$_4$-OMe-p content in the polymer was quantified by using ^{1}H NMR spectroscopy using an internal standard (ferrocene) and by comparing the integrals of the standard signal and the anisyl (An) resonances. In this way the stoichiometric allyl chloride/Sn–An = 1:1 ratio was maintained in each cycle and the activity of the polymer could be evaluated independently of small variations of the efficiency in the reactions with the Li(C$_6$H$_4$–OMe-p) derivative (step C). Table 3 displays a collection of the yields obtained in each step of the cycle represented in Scheme 2, and the tin content in the coupling product.

Table 3. Recycling experiments for copol-NB-NBSnBu$_2$(C$_6$H$_4$-OMe-p) (**6**) in the Stille reaction for entry 5 from Table 2.[a]

Cycle no.	Step A conv. [%][b]	Step B **4** yield [%]	Step C **6** yield [%]	Sn content in **13** [wt %][c]
1	81	97	100	0.03
2	68	90	91	0.03
3	79	97	97	0.02
4	90	93	96	0.07
5	90	94	–	0.07

[a] The polymers remain soluble throughout the cycles. [b] Conversions (conv.) were determined by using ^{1}H NMR spectroscopy of a sample of the reaction bulk before workup. [c] Determined by ICP–MS.

The results show that **6** is a very efficient reagent (step A) in the recycled Stille coupling and remains active throughout the cycles. Following step A, the solvent was evaporated and the polymer was precipitated in a mixture of MeOH and *n*-hexane. Almost quantitative recovery of the polymeric byproduct (**4**) was achieved (step B). The coupling product **13** was obtained by evaporation of the mother liquors and filtration of the product dissolved in *n*-hexane through silica gel. This simple procedure afforded **13** with very small tin content (Table 3). For comparison, the same Stille reaction was carried out using SnBu$_3$(C$_6$H$_4$–OMe-p) as reagent and worked up by the usual procedure, involving the transformation of the tin halide into tin fluoride (by shaking the mixture with an aqueous solution of KF), evaporation of the solvent of the organic layer, and further filtration of the residue dissolved in *n*-hexane through silica gel. In this case the coupling product **13** contained about 6 % mol of SnBu$_3$Cl (4.5 wt % tin), showing the advantage of polymer reagents for purification.

Recycling of reaction in entry 6 (Table 2): The same procedure described above was applied to polymer recycling with the reaction partners of entry 6, Table 2. The coupling reaction of allyl chloride with **7** (0.5 % mol Pd) was carried out and the polymer was reused three times with good yields in step A (60–100 %) and almost quantitative recovery (step B) and regeneration (step C) of the polymers.

Recycling of reaction in entry 2 (Table 2): This reaction was chosen because it requires more stringent conditions. As specified in Table 2, the Stille coupling was carried out at high temperature (90 °C) to ensure a fast oxidative addition of C_6F_5I. The use of this organic iodide will have the result that the initial chloride in copolymer **4** will be replaced by iodide after the first Stille step. The results over five recovery cycles (Table 4) show that, although polymer **6** remains active throughout the cycles, it gradually loses solubility, whereas reduced yields are observed in step A. This variation is not related to the exchange of Cl for I in the first cycle,[34] as step C is not negatively affected. It is plausible that conformational changes in the polynorbornene skeleton, after heating in the Stille coupling step at a higher temperature than those used in entries 5 and 6, gradually reduce the solubility of the polymers and lower the accessibility of the reagents to the active tin centers. Conformational changes upon heating have been reported for polynorbornene.[35] This reduction in activity can be compensated using an excess of polymer **6** in step A to produce **11** in good yields, as shown in independent recycling experiments.

Table 4. Recycling experiments for copol-NB-NBSnBu$_2$(C$_6$H$_4$-OMe-*p*) (**6**) in the Stille reaction for entry 2 from Table 2.[a]

Cycle no.	Step A conv. [%][b]	Step B copol-NB-NBSnBu$_2$I yield [%]	Step C **6** yield [%]
1	–	–	91[c]
2	64	72	100[d]
3	59	74	100[d]
4	40	92	80[d]
5	40	91	100[d]
6	66	88	–

[a] The composition of the starting **4** is NB/**1** = 2.5:1. [b] Reaction conditions: entry 2, Table 2. Conversions were determined by using ^{19}F NMR spectroscopy of a sample of the reaction bulk before workup. [c] Polymer synthesized from **4**, soluble in $CHCl_3$. [d] The polymers are not soluble in $CHCl_3$.

The gradual decrease in polymer solubility influences the tin content of the product. The biphenyl coupling product **11** was obtained by filtration of the solution in dioxane (to separate most of the polymer byproduct), evaporation to dryness, and addition of MeOH. Since **11** is partially soluble in methanol a first batch was obtained in this way which contains small amounts of polymer and shows tin contents from 14 % weight, in cycle 1, to 0.5 % in cycle 5. Either the second batch obtained (see the Experimental Section) or recrystallization of the first batch affords **11** with lower tin contents between 0.04 and 0.003 wt %.

It is worth noting that the yields of step A in Tables 3 and 4 have been obtained by using an equimolar Sn$-$R^2/organic halide ratio whereas it is common practice in the Stille reactions to use an excess of tin reagent (about 10–20 % excess), in spite of the fact that this complicates the contamination problem. When using our stannylated polymers the use of excess polymer can be made without this detrimental side effect, since the excess of tin reagent is separated with the byproduct. Moreover, the use of excess tin polymer eliminates the need of ^{1}H NMR spectroscopic analysis prior to each Stille reaction, and the coupling product is obtained quantitatively for the case of entry 5 in the same reaction time.

Conclusion

The vinylic copolymerization of tin-containing norbornenes with norbornene in good yield has been achieved, using [Ni(C$_6$F$_5$)$_2$(SbPh$_3$)$_2$] as catalyst. The polymers contain C_6F_5 end groups, which supports the proposal that an insertion mechanism is operating. Since the insertion of norbornene is faster than the insertion of the stannylated monomer **1**, the norbornene content of the polymer is always higher than its ratio in the monomer feed.

The copolymer (**4**) has an all-aliphatic skeleton and $-$SnBu$_2$Cl groups. It is a versatile reagent as it can be transformed by reaction with the corresponding organolithium or organomagnesium compound into new copolymers with $-$SnBu$_2$R moieties (R = aryl, vinyl, alkynyl, etc.) that can be used as coupling partners in a wide number of Stille reactions. Most importantly, these polymers are efficiently reused affording good yields in several cycles. Moreover, the use of these polynorbornene reagents in the Stille coupling provides an easy reaction workup, better separation of the halostannylated products, and low content of tin in the coupling products, thus representing a good alternative to address the problem of tin contamination.

Experimental Section

General: ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{119}Sn NMR spectra were recorded using Bruker AC-300 and ARX-300 instruments. Chemical shifts (δ) are reported in ppm and referenced to Me_4Si (^{1}H and ^{13}C), $CFCl_3$ (^{19}F), or $SnMe_4$ (^{119}Sn). All of the NMR spectra were recorded at 293 K. Elemental analyses were determined by using a Perkin–Elmer 2400 CHN microanalyzer. The tin content of the products was determined by ICP–MS in the SCAI center of the University of Burgos, using Agilent 7500i equipment; the samples were dissolved in a mixture of $HNO_3/H_2SO_4 = 7:3$ using an ETHOS SEL Milestone microwave oven. The chloro content in the polymer was determined by oxygen-flask combustion of a sample and analysis of the residue by the mercurimetric titration of chloride.[32] Size exclusion chromatography (SEC) was carried out using a Waters SEC system using a three-column bed (Styragel 7.8 × 300 mm columns: 50–100.000, 5000–500.000, and 2.000–4.000.000 D) and a Waters 410 differential refractometer. SEC samples were run in $CHCl_3$ at 313 K and calibrated to polystyrene standards. Solvents were dried over CaH_2 or Na, distilled, and deoxygenated prior to use. Norbornadiene, $SnBu_2Cl_2$, and the organic halides were purchased from Aldrich or Acros. The compounds

$SnBu_2H_2$,[36] **3**,[26,37] [{Pd($AsPh_3$)(μ-Br)(C_6F_5)}$_2$],[38] and [{Pd(η^3-C_3H_5)(μ-Cl)}$_2$][39] were prepared according to the literature.

Dibutylchlorostannylnorbornene (1): $SnBu_2H_2$ (0.962 g, 4.093 mmol) was added dropwise to a mixture of norbornadiene (2.263 g, 24.56 mmol), AIBN (0.0672 g, 0.409 mmol), and $SnBu_2Cl_2$ (1.244 g, 4.093 mmol). The reaction mixture was maintained in a water bath at room temperature for 12 h. The product was obtained as a yellow liquid after pumping off the excess of norbornadiene. Isolated yield: 2.427 g (82 %). The product is a mixture of four isomers **1a–d**.

Compound 1a: ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 6.06$ (m, $J = 2.7$, 6.0 Hz, 1 H; H^6), 5.94 (m, $J = 2.7$, 6.0 Hz, 1 H; H^5), 3.07 (br, 1 H; H^1), 3.04 (br, 1 H; H^4), 1.97 (m, 1 H; H^3), 1.35 (m, 1 H; H^7), 1.30 (m, 1 H; H$^{3'}$), 1.15 (m, 2 H; H^2, H$^{7'}$), 1.81–1.05 (m; 12 H$_{Bu}$), 0.87 ppm (t, 6 H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 136.1$ (s, $^3J_{Sn,C} = 63.7$ Hz; C^6), 133.7 (s; C^5), 48.2 (s, $^3J_{Sn,C} = 0$ Hz; C^7), 44.6 (s; C^1), 42.8 (s, $^3J_{Sn,C} = 22.6$ Hz; C^4), 28.5 (s; C^2), 27.9 (s; CH_2), 27.5 (s; C^3), 27.0 (s; CH_2), 17.1 (s; CH_2-Sn), 13.5 ppm (s; CH_3); ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): $\delta = 148.8$ ppm (s).

Compound 1b: ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 6.10$ (m, $J = 3.0$, 5.4 Hz, 1 H; H^5), 6.03 (m, $J = 3.0$, 5.4 Hz, 1 H; H^6), 3.20 (br, 1 H; H^1), 3.00 (br, 1 H; H^4), 2.10 (m, 1 H; H^3), 1.94 (m, 1 H; H^2), 1.55 (m, 1 H; H^7), 1.30 (m, 1 H; H$^{3'}$), 1.13 (m, 1 H; H$^{7'}$), 1.05–1.81 (m; 12 H$_{Bu}$), 0.87 ppm (t, 6 H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 137.0$ (s; C^5), 135.0 (s, $^3J_{Sn,C} = 33.4$ Hz; C^6), 49.9 (s, $^3J_{Sn,C} = 55.3$ Hz; C^7), 45.3 (s; C^1), 41.8 (s, $^3J_{Sn,C} = 22.6$ Hz; C^4), 30.8 (s; C^2), 27.9 (s; CH_2), 27.4 (s; C^3), 27.0 (s; CH_2), 17.1 (s; CH_2-Sn), 13.5 ppm (s; CH_3); ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): $\delta = 140.3$ ppm (s).

Compound 1c: ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 6.11$ (m, 2 H; H^5, H^6), 3.26 (br, 2 H; H^4, H^1), 2.27 (m, 1 H; H^7), 1.81–1.05 (m, 16 H; 12 H$_{Bu}$, H^3, H$^{3'}$, H^2, H$^{2'}$), 0.87 ppm (t, 6 H; CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 138.0$ (s; C^5, C^6), 45.6 (s; C^1, C^4), 32.5 (s; C^7), 27.9 (s; CH_2), 27.0 (s; CH_2), 25.2 (s; C^2), 25.1 (s; C^3), 17.6 (s; CH_2-Sn), 13.5 ppm (s; CH_3); ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): $\delta = 133.2$ ppm (s) (the assignment of this signal could be reversed).

Compound 1d: ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.81$–1.05 (m, 21 H; 12 H$_{Bu}$, H$^{1-7}$), 0.87 ppm (t, 6 H; CH_3); ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): $\delta = 142.1$ ppm (s) (the assignment of this signal could be reversed).

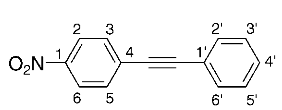
Copol-NB-NBSnBu$_2$Cl (4): Compound **1** (0.670 g, 1.853 mmol), a solution of norbornene in CH_2Cl_2 (0.65 mL, 2.88 M, 1.853 mmol; the solution of norbornene was titrated by using ^{1}H NMR spectroscopy with $C_6H_3Br_3$ as internal standard) and dry CH_2Cl_2 (1.85 mL) were mixed in an oven-dried Schlenk flask under nitrogen. A solution of **3** (0.0407 g, 0.037 mmol) in CH_2Cl_2 (1 mL) was then added. After being stirred for 24 h at room temperature, the copolymer was precipitated by pouring the mixture into MeOH (50 mL). The MeOH was decanted off and the copolymer was filtered, washed with MeOH, and air-dried. Isolated yield: 0.611 g (72 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 2.6$–0.7 ppm (br; H$_{Bu}$, H$^{1-7}$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 54.5$–50.0 (br; C^{5,6}), 41.5–39.0 (br; C^{1,4}), 38.0–35.0 (br; C^7), 32.5–29.0 (br; C^{2,3}), 27.9 (s; Bu: -CH_2-*C*H$_2$-CH_2-), 27.0 (s; Bu: -*C*H$_2$-CH_3), 16.8 (br; Bu: -*C*H$_2$-Sn), 13.6 ppm (s; Bu: *C*H$_3$-); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -133.8$, -140.6 (br; F$_{ortho}$), -158.4 (br; F$_{para}$), -163.4 ppm (br; F$_{meta}$); ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): $\delta = 142.3$ ppm (br).

The same procedure was used for the experiments collected in Table 1. Large-scale syntheses were carried out just by scaling up reactants and solvents.

Functionalization of polymers—synthesis of 6: A solution of butyllithium in *n*-hexane (6.77 mL, 1.6 M, 10.824 mmol) was added to THF (46 mL) at 0 °C. The mixture was cooled to −90 °C and 4-bromoanisole (1.850 g, 9.89 mmol) in THF (15 mL) was added over a 5 min period at that temperature. The temperature was allowed to rise to −50 °C and stirring continued for 15 min.[40] Then **4** was added (2.550 g, 4.920 mmol) and the reaction mixture was allowed to slowly warm to room temperature and stirred for 24 h. After that time, water (1 mL) was added and THF was pumped off. The residue was washed with acidic MeOH and stirred for 30 min. The MeOH was then decanted off and the resulting copolymer was filtered, washed with MeOH and air-dried. Isolated yield: 2.802 g (96 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 7.4$ (br, 2 H; H$_{ortho}$), 6.8 (br, 2 H; H$_{meta}$), 3.7 (s, 3 H; OCH_3), 2.8–0.7 ppm (br; H$_{Bu}$, H$^{1-7}$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): $\delta = 159.6$ (s; *C*$_{para}$-OCH_3), 137.7 (s; C$_{ortho}$), 133.1 (s; C$_{ipso}$-Sn), 113.9 (s; C$_{meta}$), 54.8 (s; OCH_3), 53.0–50.0 (br; C^{5,6}), 48.5–46.5 (br; C^{1,4}), 40.5–39.0 (br; C^7), 36.5–34.1 (br; C^{1,2}), 29.2 (s; Bu: -CH_2-*C*H$_2$-CH_2-), 27.6 (s; Bu: -*C*H$_2$-CH_3), 13.7 (s; Bu: *C*H$_3$-), 9.2 ppm (br; Bu: -*C*H$_2$-Sn); ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): $\delta = -45.5$ ppm (br).

The other functionalized copolymers **5** and **7–9** (Table 2 and Eq. (3)) and the recycled one according to step C in Scheme 2 were prepared following the same procedure but using the corresponding lithium or magnesium derivatives. Li(*p*-C_6H_4F)[41] and Li(*p*-CF_3–C_6H_4)[42] were prepared in diethyl ether by mixing the corresponding bromo derivative and butyllithium at −40 °C and stirring for 1 h. Li($C_2C_6H_4$) is commercially available (Aldrich), but it was prepared in diethyl ether by mixing phenylacetylene and butyllithium at −40 °C and stirring for 1 h. CH_2=CH–MgBr was prepared following the procedure in the literature.[43] Spectroscopic data for copolymers **5** and **7–9** are included in the Supporting Information.

Stille reactions—preparation of *p*-NO$_2$-C$_6$H$_4$-C≡C-C$_6$H$_5$ (12):[44] A 5 mm NMR spectroscopy tube was charged under N_2 with copol-NB-NBSnBu$_2$-C≡C-C_6H_5 (**9**) (0.0300 g, 0.058 mmol; the molar amount of Sn–R groups was determined by ^{1}H NMR spectroscopy titration using an internal standard, as described in the text and the Supporting Information), *p*-NO$_2$-C_6H_4I (0.0115 g, 0.046 mmol), $CDCl_3$ (0.4 mL) and [{Pd($AsPh_3$)(μ-Br)(C_6F_5)}$_2$] (0.0015 g, 0.0012 mmol). The reaction mixture was heated at 50 °C for 24 h and the formation of *p*-NO$_2$-C_6H_4-C≡C-C_6H_5 was observed by ^{1}H NMR spectroscopy. Yield was calculated by integration of the ^{1}H NMR signals (100 % yield). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 8.23$ (m, 2 H; H^{2,6}), 7.67 (m, 2 H; H^{3,5}) 7.56 (m, 2 H; H$^{2',6'}$), 7.35 ppm (m, 3 H; H$^{3',4',5'}$).



The other Stille reactions were carried out in a similar way starting from the corresponding copolymer, hydrocarbyl halide, and catalysts as collected in Table 2. Compounds **10**,[45] **11**,[46] **13**,[47] **14**,[48] **15**,[49] **16**,[50] **17**,[51] and **18**[52] have been described before. Nonetheless spectroscopic data are included below or in the Supporting Information.

Synthesis of *p*-methoxyallyl benzene (13):[47] Copol-NB-NBSnBu$_2$(C_6H_4-OMe-*p*) (**6**, 4.600 g, 5.700 mmol Sn-(C_6H_4-OMe-*p*); the molar amount of Sn-(C_6H_4-OMe-*p*) groups was determined by using ^{1}H NMR spectroscopy titration using an internal standard, as described in the text and the Supporting Information), allylchloride (0.4362 g, 5.700 mmol), $CHCl_3$ (110 mL), benzoquinone (0.0062 g, 0.057 mmol), and a solution of [{Pd(η^3-C_3H_5)(μ-Cl)}$_2$] (0.0104 g, 0.028 mmol) in $CHCl_3$ (1 mL) were added to a Schlenk flask successively under N_2. The reaction mixture was heated at 50 °C for 24 h. After that time, a small portion was taken and the formation of CH_2=CH-CH_2-(C_6H_4-OMe-*p*) was observed by using ^{1}H NMR spectroscopy (crude yield: 81 %; calculated by integration of the allylic signals of the allylchloride and the cross-coupling product). The solvent was the evaporated to around 10 mL and a mixture of *n*-hexane (50 mL) and MeOH (50 mL) was added. The copolymer copol-NB-NBSnBu$_2$Cl was filtered, washed with MeOH, and dried in vacuum to yield 4.003 g (97 % yield). The filtrate was concentrated to 5 mL, treated with activated charcoal and filtered through silica gel. After distillation to remove the solvents, **13** was obtained as an orange liquid (0.674 g, 80 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 7.12$ (m, $J = 8.76$ Hz, 2 H; H^{2,6}), 6.86 (m, $J = 8.76$ Hz, 2 H; H^{3,5}), 5.98 (m, $J = 16.7$, 10.5, 6.6 Hz, 1 H; CH_2=C*H*-CH_2-), 5.09 (d, $J = 16.7$ Hz, 1 H; C*H*H=CH-CH_2-), 5.06 (d, $J = 10.5$ Hz, 1 H; CH*H*=CH-CH_2-), 3.82 (s, 3 H; OCH_3), 3.34 ppm (d, $J = 6.6$ Hz, 2 H; CH_2=CH-C*H*$_2$-).

Synthesis of 2,3,4,5,6-pentafluoro-4′-methoxybiphenyl (11):[46] A Schlenk flask was charged under N_2 with **6** (2.000 g, 3.700 mmol Sn-C_6H_4-OMe-*p*; the molar amount of Sn-(C_6H_4-OMe-*p*) groups was determined by using ^{1}H NMR spectroscopy titration using an internal standard, as described in the text and the Supporting Information), C_6F_5I (0.875 g, 2.960 mmol), 1,4-dioxane (50 mL), and finally a solution of [{Pd($AsPh_3$)(μ-Br)(C_6F_5)}$_2$] (0.0976 g, 0.074 mmol) in 1,4-dioxane (1 mL). The reaction mixture was heated at 90°C for 3 days. After that time it was cooled down and a small portion was taken and the formation of **11** was observed by using ^{19}F NMR spectroscopy (crude yield: 69%; calculated by integration of the F_{ortho} signals of the C_6F_5I and the cross-coupling product). The insoluble copolymer copol-NB-NBSnBu_2I was filtered, washed with MeOH, and dried under vacuum to yield 1.939 g (94%). The filtrate was evaporated to dryness and the yellow solid that appeared (**11**) was washed with MeOH and air dried to yield 0.4467 g. The filtrate was concentrated to 5 mL to obtain a second batch of a yellow solid (**11**), which was washed with MeOH and air-dried; isolated yield: 0.3555 g (36%). The first batch was contaminated with small amounts of polymer, and it was recrystallized from hot methanol; isolated yield: 0.2133 g (22%). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 7.35$ (m, $J = 10.0$ Hz, 2H; $H^{2,6}$), 7.05 (m, $J = 10.0$ Hz, 2H; $H^{3,5}$), 3.85 ppm (s, 3H; OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -144.1$ (m, 2F; F_{ortho}), -156.8 (t, 1F; F_{para}), -163.9 ppm (m, 2F; F_{meta}); elemental analysis calcd (%) for $C_{13}H_7F_5O$: C 56.95, H 2.57; found: C 56.70, H 2.72.

Acknowledgements

Financial support from the Spanish MEC (DGI, grant CTQ2007-67411/BQU; Consolider Ingenio 2010, grant INTECAT, CSD2006-0003; FPU fellowship to N.C.), and the Junta de Castilla y León (project VA117A06) is gratefully acknowledged.

---

[1] T. N. Mitchell in *Metal Catalyzed Cross-Coupling Reactions* (Eds.: A. Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, Chapter 3.

[2] V. Farina, V. Krishanamurthy, W. J. Scott, *The Stille Reaction*, Wiley, New York, **1998**.

[3] R. D. McCullough, P. C. Ewbank, R. S. Loewe, *J. Am. Chem. Soc.* **1997**, *119*, 633–634.

[4] a) K. C. Nicolaou, P. G. Bulger, D. E. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; b) H. W. Lam, G. Pattenden, *Angew. Chem.* **2002**, *114*, 526–529; *Angew. Chem. Int. Ed.* **2002**, *41*, 508–511; c) K. C. Nicolaou, J. Xu, F. Murphy, S. Barluenga, O. Baudoin, H. Wei, D. L. F. Gray, T. Ohshima, *Angew. Chem.* **1999**, *111*, 2599–2604; *Angew. Chem. Int. Ed.* **1999**, *38*, 2447–2451; d) K. C. Nicolaou, T. K. Chakraborty, A. D. Piscopio, N. Minowa, P. Bertinato, *J. Am. Chem. Soc.* **1993**, *115*, 4419–4420.

[5] a) P. Espinet, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 4808–4839; *Angew. Chem. Int. Ed.* **2004**, *43*, 4704–4734; b) J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524; c) D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1978**, *100*, 3636–3638.

[6] D. Stien, S. Gastaldi, *J. Org. Chem.* **2004**, *69*, 4464–4470.

[7] a) K. Olofsson, S.-Y. Kim, M. Larhed, D. P. Curran, A. Hallberg, *J. Org. Chem.* **1999**, *64*, 4539–4541; b) M. Larhed, M. Hoshino, S. Hadida, D. P. Curran, A. Hallberg, *J. Org. Chem.* **1997**, *62*, 5583–5587.

[8] D. A. Powell, T. Maki, G. C. Fu, *J. Am. Chem. Soc.* **2005**, *127*, 510–511.

[9] a) W. P. Gallagher, I. Terstiege, R. E. Maleczka, Jr., *J. Am. Chem. Soc.* **2001**, *123*, 3194–3204; b) R. E. Maleczka, Jr., W. P. Gallagher, *Org. Lett.* **2001**, *3*, 4173–4176; c) R. E. Maleczka, Jr., W. P. Gallagher, I. Terstiege, *J. Am. Chem. Soc.* **2000**, *122*, 364–385.

[10] a) P. Boussaguet, B. Delmond, G. Dumartin, M. Pereyre, *Tetrahedron Lett.* **2000**, *41*, 3377–3380; b) E. J. Enholm, J. P. Schulte II, *Org. Lett.* **1999**, *1*, 1275–1277; c) E. J. Enholm, M. E. Gallagher, K. M. Moran, J. S. Lombardi, J. P. Schulte II, *Org. Lett.* **1999**, *1*, 689–691; d) J. Junggebauer, W. P. Neumann, *Tetrahedron* **1997**, *53*, 1301–1310; e) G. Dumartin, G. Ruel, J. Kharboutli, B. Delmond, M.-F. Connil, B. Jousseaume, M. Pereyre, *Synlett* **1994**, 952–954; f) D. P. Dygutsch, W. P. Neumann, M. Peterseim, *Synlett* **1994**, 363–365; g) G. Ruel, N. Ke, G. Dumartin, B. Delmond, M. Pereyre, *J. Organomet. Chem.* **1993**, *444*, C18–C20; h) M. Harendza, K. Lessmann, W. P. Neumann, *Synlett* **1993**, 283–285; i) C. Bokelmann, W. P. Neumann, M. Peterseim, *J. Chem. Soc. Perkin Trans. 1* **1992**, 3165–3166; j) M. Gerlach, F. Jördens, H. Kuhn, W. P. Neumann, M. Peterseim, *J. Org. Chem.* **1991**, *56*, 5971–5972; k) U. Gerigk, M. Gerlach, W. P. Neumann, R. Vieler, V. Weintritt, *Synthesis* **1990**, 448–452; l) D. E. Bergbreiter, S. A. Walker, *J. Org. Chem.* **1989**, *54*, 5138–5141.

[11] a) L. Angiolini, D. Caretti, L. Mazzocchetti, E. Salatelli, R. Willem, M. Biesemans, *J. Organomet. Chem.* **2006**, *691*, 3043–3052; b) C. Camacho-Camacho, M. Biesemans, M. Van Poek, F. A. G. Mercier, R. Willem, K. Darriet-Jambert, B. Jousseaume, T. Toupance, U. Schneider, U. Gerigk, *Chem. Eur. J.* **2005**, *11*, 2455–2461.

[12] J.-M. Chrétien, F. Zammattio, D. Gauthier, E. Le Grognec, M. Paris, J.-P. Quintard, *Chem. Eur. J.* **2006**, *12*, 6816–6828.

[13] J.-M. Chrétien, F. Zammattio, D. Gauthier, E. Le Grognec, M. Paris, B. Cahingt, G. Montavon, J.-P. Quintard, *J. Org. Chem.* **2005**, *70*, 2870–2873.

[14] D. H. Hunter, C. McRoberts, *Organometallics* **1999**, *18*, 5577–5583.

[15] A. G. Hernán, J. D. Kilburn, *Tetrahedron Lett.* **2004**, *45*, 831–834.

[16] a) J.-M. Chrétien, A. Mallinger, F. Zammattio, E. Le Grognec, M. Paris, G. Montavon, J.-P. Quintard, *Tetrahedron Lett.* **2007**, *48*, 1781–1785; b) K. C. Nicolaou, N. Winssinger, J. Pastor, F. Murphy, *Angew. Chem.* **1998**, *110*, 2677–2680; *Angew. Chem. Int. Ed.* **1998**, *37*, 2534–2537; c) H. Kuhn, W. P. Neumann, *Synlett* **1994**, 123–124.

[17] a) A. G. Hernán, P. N. Horton, M. B. Hursthouse, J. D. Kilburn, *J. Organomet. Chem.* **2006**, *691*, 1466–1475; b) A. G. Hernán, V. Guillot, A. Kuvshinov, J. D. Kilburn, *Tetrahedron Lett.* **2003**, *44*, 8601–8603.

[18] A. G. Davies, *Organotin Chemistry*, Wiley-VCH, Weinheim, **2004**, Chapter 23.

[19] W. P. Neumann, J. Pedain, *Tetrahedron Lett.* **1964**, *5*, 2461–2465.

[20] J. D. Kennedy, H. G. Kuivila, F. L. Pelczar, J. L. Considine, *J. Organomet. Chem.* **1973**, *61*, 167–177.

[21] H. G. Kuivila, J. D. Kennedy, R. Y. Tien, I. J. Tyminski, F. L. Pelczar, O. R. Khan, *J. Org. Chem.* **1971**, *36*, 2083–2088.

[22] a) A. Rahm, J. Grimeau, M. Petraud, B. Barbe, *J. Organomet. Chem.* **1985**, *286*, 297–304; b) D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C.-H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, R. H. Sarma, *J. Am. Chem. Soc.* **1974**, *96*, 1640–1642.

[23] For Review accounts see: a) B. L. Goodall in *Late Transition Metal Polymerization Catalysis* (Eds.: B. Rieger, L. Saunders Baugh, S. Kacker, S. Striegler), Wiley-VCH, Weinheim, **2003**, Chapter 4; b) C. Janiak, P. G. Lassahn, *J. Mol. Catal. A* **2001**, *166*, 193–209.

[24] a) M. Yamashita, I. Takamiya, K. Jin, K. Xozaki, *Organometallics* **2006**, *25*, 4588–4595; b) S. Kaita, K. Matsushita, M. Tobita, Y. Maruyama, Y. Wakatsuki, *Macromol. Rapid Commun.* **2006**, *27*, 1752–1756; c) E. S. Finkelshtein, K. L. Makovetskii, M. L. Gringolts, Y. V. Rogan, T. G. Golenko, L. E. Starannikova, Y. P. Yampolskii, V. P. Shantarovich, T. Suzuki, *Macromolecules* **2006**, *39*, 7022–7029; d) L. Y. Wang, Y. F. Li, F. M. Zhu, Q. Wu, *Eur. Polym. J.* **2006**, *42*, 322–327; e) D. A. Barnes, G. M. Benedikt, B. L. Goodall, S. S. Huang, H. A. Kalamarides, S. Lenhard, L. H. McIntosh, K. T. Selvy, R. A. Shick, L. F. Rhodes, *Macromolecules* **2003**, *36*, 2623–2632; f) J. Lipian, R. A. Mimma, J. C. Fondran, D. Yandulov, R. A. Shick, B. L. Goodall, L. F. Rhodes, *Macromolecules* **2002**, *35*, 8969–8977; g) A. D. Hennis, J. D. Polley, G. S. Long, A. Sen, D. Yandulov, J. Lipian, G. M. Benedikt, L. F. Rhodes, J. Huffman, *Organometallics* **2001**, *20*, 2802–2812.

[25] L. F. Rhodes, A. Bell, S. Jayaraman, J. H. Lipian, B. L. Goodall, R. A. Shick, Photoresist Compositions Comprising Polycyclic Polymers with Acid Labile Pendant Groups, U.S. Patent 6,232,417, May 15, **2001**.

[26] J. A. Casares, P. Espinet, J. M. Martín-Alvarez, J. M. Martínez-Ilarduya, G. Salas, *Eur. J. Inorg. Chem.* **2005**, 3825–3831.

[27] a) A. C. Albéniz, P. Espinet, Y.-S. Lin, *Organometallics* **1996**, *15*, 5010–5017; b) A. C. Albéniz, P. Espinet, Y.-S. Lin, *Organometallics* **1997**, *16*, 4138–4144; c) A. C. Albéniz, P. Espinet, Y.-S. Lin, *Organometallics* **1997**, *16*, 5964–5973; d) A. C. Albéniz, P. Espinet, Y. Jeannin, M. Philoche-Levisalles, B. Mann, *J. Am. Chem. Soc.* **1990**, *112*, 6594–6600; e) A. C. Albéniz, P. Espinet, C. Foces-Foces, F. H. Cano,

Organometallics **1990**, *9*, 1079–1085; f) R. Usón, J. Forniés, P. Espinet, E. Lalinde, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1982**, 2389–2395.

[28] W.-J. Huang, F.-C. Chang, P. P.-J. Chu, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 2554–2563.

[29] M. Arndt, R. Engehausen, W. Kaminsky, K. Zoumis, *J. Mol. Catal. A* **1995**, *101*, 171–178.

[30] a) C. Karafilidis, K. Angermund, B. Gabor, A. Rufinska, R. J. Mynott, G. Breitenbruch, W. Thiel, G. Fink, *Angew. Chem.* **2007**, *119*, 3819–3823; *Angew. Chem. Int. Ed.* **2007**, *46*, 3745–3749; b) C. Karafilidis, H. Hermann, A. Rufinska, B. Gabor, R. J. Mynott, G. Breitenbruch, C. Weidenthaler, J. Rust, W. Joppek, M. S. Brookhart, W. Thiel, G. Fink, *Angew. Chem.* **2004**, *116*, 2498–2500; *Angew. Chem. Int. Ed.* **2004**, *43*, 2444–2446.

[31] W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Macromol. Symp.* **1991**, *41*, 83–93.

[32] The chloro content in the polymer was determined by oxygen-flask combustion of a sample and analysis of the residue by the mercurimetric titration of chloride: D. C. White, *Microchim. Acta* **1961**, 449–456.

[33] A. C. Albéniz, P. Espinet, B. Martín-Ruiz, *Chem. Eur. J.* **2001**, *7*, 2481–2489.

[34] Copol-NB-NBSnBu$_2$I was synthesized from **4** by treatment with KI. Copolymer **6** was synthesized either from **4** or from copol-NB-NBSnBu$_2$I with Li(C$_6$H$_4$-OMe-*p*) [Eq. (3)] in similar yields and Sn-(C$_6$H$_4$-OMe-*p*) incorporation.

[35] P. P. Chu, W.-J. Huang, F.-C. Chang, S. Y. Fan, *Polymer* **2000**, 401–404.

[36] G. J. M. Van Der Kerk, J. G. Noltes, J. G. A. Luijten, *J. Appl. Chem.* **1957**, *7*, 366–374.

[37] a) A. Arcas, P. Royo, *Inorg. Chim. Acta* ***1978***, *30*, 205–207; b) G. Lopez, G. García, G. Sánchez, J. García J. Ruiz, J. A. Hermoso, A. Vegas, M. Martínez-Ripoll, *Inorg. Chem.* **1992**, *31*, 1518–1523.

[38] A. C. Albéniz, P. Espinet, R. López-Fernández, *Organometallics* **2003**, *22*, 4206–4212.

[39] Y. Tatsuno, T. Yoshida, Seiotsuka in *Inorganic Syntheses, Vol. 19* (Ed.: D. F. Shriver), Wiley-Interscience, New York, **1979**, p. 220–221.

[40] L. Brandsma, V. Hermann, *Preparative Polar Organometallic Chemistry 1*, Springer-Verlag, Berlin Heidelberg, **1989**, p. 189–190.

[41] M. Scholosser, V. Ladenberger, *J. Organomet. Chem.* **1967**, *8*, 193–197.

[42] Y. Yu, J. Sun, J. Chen, *J. Organomet. Chem.* **1997**, *533*, 13–23.

[43] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, R. Cserr, *J. Org. Chem.* **1957**, *22*, 1602–1605.

[44] CAS registry number: 1942–30–9. a) E. M. Beccalli, A. Manfredi, A. Marchesini, *J. Org. Chem.* **1985**, *50*, 2372–2375; b) W. E. McEwen, A. P. Guzikowski, A. P. Wolf, *J. Fluorine Chem.* **1984**, *25*, 169–193.

[45] a) A. C. Albéniz, P. Espinet, Y.-S. Lin, *Organometallics* **1997**, *16*, 5964–5973; b) A. C. Albéniz, P. Espinet, Y.-S. Lin, A. G. Orpen, A. Martin, *Organometallics* **1996**, *15*, 5003–5009.

[46] Q.-Y. Chen, Z.-T. Li, *J. Org. Chem.* **1993**, *58*, 2599–2604.

[47] CAS registry number: 140–67-0. a) P. Gomes, C. Gosmini, J. Périchon, *J. Org. Chem.* **2003**, *68*, 1142–1145; b) R. C. Haley, J. A. Miller, H. C. S. Wood, *J. Chem. Soc. C* **1969**, 264–268.

[48] CAS registry number: 1737-16-2. a) P. Gomes, C. Gosmini, J. Périchon, *J. Org. Chem.* **2003**, *68*, 1142–1145; b) P. Chevalier, D. Sinou, G. Descotes, *Bull. Soc. Chim. Fr.* **1975**, 2254–2258.

[49] CAS registry number: 1813–97–4. a) P. Gomes, C. Gosmini, J. Périchon, *J. Org. Chem.* **2003**, *68*, 1142–1145; b) M. M. Martin, G. J. Gleicher, *J. Am. Chem. Soc.* **1964**, *86*, 233–238.

[50] CAS registry number: 611-94-9. a) S. S. Kulp, M. J. McGee, *J. Org. Chem.* **1983**, *48*, 4097–4098.

[51] CAS registry number: 345-83-5. a) S. S. Kulp, M. J. McGee, *J. Org. Chem.* **1983**, *48*, 4097–4098.

[52] a) S. Nahm, S. M. Weinreb, *Tetrahedron Lett.* **1981**, *22*, 3815–3818.

Received: March 26, 2008