Articles

Synthesis of Poly(2-substituted-1-propenylene)s from Allylic Arsonium Ylides

Régis Mondière,[†] Jean-Philippe Goddard,[†] Géraldine Carrot,[‡] Thierry Le Gall,*[,†] and Charles Mioskowski*[,†,§]

CEA-Saclay, Service de Marquage Moléculaire et de Chimie Bioorganique, Bât. 547, 91191 Gif-sur-Yvette, France; CEA-Saclay, Laboratoire Léon Brillouin CEA-CNRS, 91191 Gif-sur-Yvette, France; and Laboratoire de Synthèse Bio-Organique, UMR CNRS 7514, Faculté de Pharmacie, Université Louis Pasteur, 74 route du Rhin, B.P. 24, 67401 Illkirch, France

Received November 10, 2004; Revised Manuscript Received November 19, 2004

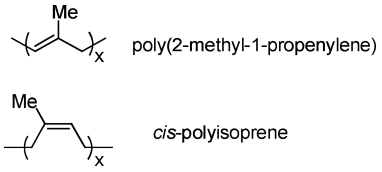
ABSTRACT: The polymerization of several allylic triphenylarsonium ylides, which contain a pendant R group at the 2-position, in the presence of triethylborane, is described. Three initial molar ratios of ylide to triethylborane (15, 30, 60) were used, leading to different degrees of polymerization. The ylide was generated from the corresponding arsonium salt, in THF at −78 °C, using either *tert*-butyllithium (when R = alkyl) or lithium hexamethyldisilazide (when R = tBuMe$_2$SiOCH$_2$CH$_2$−) as the base. After addition of triethylborane at 0 °C, the deep-red solution of ylide was readily discolored. Then oxidation of the resulting polymeric borane led to linear skipped polyenes containing a terminal alcohol function. These polymers can be called poly(2-substituted-1-propenylene)s. Molecular weights have been determined from both ^{1}H NMR analyses and size exclusion chromatography (SEC). In most cases, the molecular weight of the polymers increases linearly with the initial ylide/triethylborane molar ratio, which gives credit to a controlled polymerization process. Block copolymers were also obtained from triethylborane by successive additions of two different 2-substituted allylic arsonium ylides, followed by oxidation (yield: 62−85%).

Introduction

Developing new methods of polymerization is of great interest because it can provide access to new polymeric materials that may display unprecedented properties and lead to useful applications. New methods are especially attractive if they proceed with a good control of the chain growth. Indeed, this is the key for the preparation of elaborated materials such as block copolymers.[1] Block copolymers can self-assemble, leading to various specific morphologies, such as micelles, rods, or cylinders. These properties are useful for various applications.[2]

Boron compounds have been shown to induce the polymerization of diazo compounds,[3] and more recently, a living polymethylene synthesis based on the polyhomologation of boron compounds with dimethylsulfoxonium methylide was reported.[4] In the course of a study of the reactivity of boron compounds with various nucleophilic species having an α-leaving group, we found that the ylide derived from methallyl triphenylarsonium tetrafluoroborate polymerized efficiently in the presence of trialkylboranes.[5] The synthesized polymer, poly(2-methyl-1-propenylene), is a skipped polyene, in which methyl-substituted double bonds are separated by one methylene group (Scheme 1). In the structurally related polyisoprene, double bonds are separated by two methylene groups. Moreover, in contrast with the well-known polymerization of alkenes which proceeds by successive elongations of two atoms in a carbon chain, the polymerization leading to poly(2-methyl-1-propenylene) proceeds by successive chain elongations of three carbon atoms at a time.

Scheme 1



In the present report, we show that this new polymerization method can be applied to the preparation of other poly(2-substituted-1-propenylene)s. Thus, we describe the synthesis of several linear polymers containing various pendant groups by treatment of the corresponding allylic triphenylarsonium ylides substituted at the 2-position with triethylborane. Notably, a polymer containing oxygenated pendant groups was synthesized. Moreover, we show that block copolymers can be prepared using sequential additions of differently substituted arsonium ylides.

Results and Discussion

Synthesis of the 2-Substituted Allylic Arsonium Salts. The allylic arsonium salts **2a**−**d** employed in this

[†] Service de Marquage Moléculaire et de Chimie Bioorganique.
[‡] Laboratoire Léon Brillouin.
[§] Université Louis Pasteur.
* Corresponding author: e-mail legall@dsvidf.cea.fr or mioskow@aspirine.u-strasbg.fr.

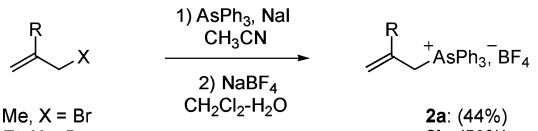
10.1021/ma047693e CCC: $30.25
Published on Web 01/14/2005

Table 1. Preparation of Homopolymers 3a−d from Ylides Derived from Arsonium Salts 2a−d and Triethylborane

entry	starting material[a]	DP_{calcd}[b]	DP[c] (NMR)	DP[d] (SEC)	M_n[d] (SEC)	PDI[d] (SEC)	yield[e] (%)
1	**2a**	5	7.3	10.2	595	1.58	79
2	**2a**	10	14.1	10.3	604	1.62	77
3	**2a**	20	30.7	28.2	1568	1.21	76
4	**2b**	5	9.0	13.1	939	1.31	77
5	**2b**	10	17.1	14.3	1015	1.23	85
6	**2b**	20	40.1	33.1	2295	1.55	72
7	**2c**	5	6.5	8.1	1049	1.28	62
8	**2c**	10	14.8	11.3	1446	1.28	64
9	**2c**	20	23.2	18.9	2393	1.80	47
10	**2d**	5	6.5	5.1	1065	1.36	65
11	**2d**	10	7.7	5.5	1135	1.76	37
12	**2d**	20	14.4	8.9	1806	1.72	37

[a] Base: *t*-BuLi (entries 1−9) or LHMDS (entries 10−12). [b] Degree of polymerization, as calculated from the molar ratio of ylide to triethylborane ($DP_{calcd} = n/3$). [c] DP determined from ^1H NMR spectra integrations. [d] DP, M_n (number-averaged molecular weight), and PDI (polydispersity index) determined from SEC coupled with two-angle laser light scattering (TALLS). [e] Yield of chromatographed polymer.

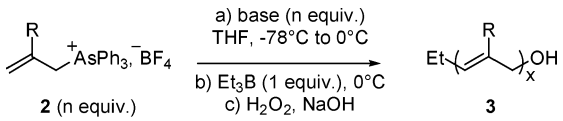
Scheme 2



1a: R = Me, X = Br
1b: R = Et, X = Br
1c: R = hexyl, X = Cl
1d: R = $(CH_2)_2OSiMe_2t$-Bu, X = Cl

2a: (44%)
2b: (59%)
2c: (46%)
2d: (61%)

Scheme 3



2 (n equiv.) **3**

2a, **3a**: R = Me
2b, **3b**: R = Et
2c, **3c**: R = hexyl
2d, **3d**: R = $(CH_2)_2OSiMe_2t$-Bu

study have not been previously described. They were prepared from the corresponding allylic bromides or chlorides **1a**−**d** as depicted in Scheme 2.

The arsonium salts **2a**−**d** were prepared as described in Scheme 2. Preliminary tests had shown that the reaction of allylic halides with triphenylarsine at room temperature in acetonitrile proceeded very slowly, necessitating several weeks to go to completion, even when a large excess of triphenylarsine was employed. On the other hand, refluxing the mixture led to the degradation of the products. Compound **2a** was prepared in 44% yield by heating, at 90 °C for 2 days, a suspension of methallyl bromide and triphenylarsine in acetonitrile, followed by stirring vigorously a dichloromethane solution of the crude product in the presence of an aqueous solution of sodium tetrafluoroborate. Slightly different, satisfactory conditions were employed for arsonium salts **2b**−**d**. Thus, a suspension of halide, triphenylarsine, and sodium iodide in acetonitrile was heated at 40 °C for 4 days. Treatment with excess sodium tetrafluoroborate then led to the corresponding allylic arsonium tetrafluoroborate, which was purified either by recrystallization or by silica gel chromatography. The tetrafluoroborate salts were found to be more conveniently purified than their halide salts counterparts.[6] The yields were 44−61%.

Polymerization of the 2-Substituted Allylic Arsonium Ylides. In each case, the ylide was generated by addition of a base to a suspension of the corresponding salt in THF.[7] It was directly reacted with triethylborane. It should be pointed out that if all the base is not completely consumed during the generation of the ylide, then the remainder would react with the boron compound, thus inactivating the polymerization catalyst and stopping the reaction. Hence, the salt employed in this process should be very pure.

The polymerization of the ylides derived from arsonium salts **2a**−**c**, which contain an alkyl group at the 2-position, was performed at first (Scheme 3; Table 1, entries 1−9).[8]

Three initial molar ratios of ylide to triethylborane, n = 15, 30, and 60, were used, corresponding to theoretical degrees of polymerization (DP) 5, 10, and 20, respectively, assuming that the polymerization can occur along the three substituents on the boron atom. The ylide was generated in THF at −78 °C using *tert*-butyllithium as the base. After warming to 0 °C, a deep-red solution of ylide was obtained in each case. Triethylborane (1 M solution in hexane) was then added in one shot, and an instantaneous discoloration of the solution was observed, indicating that all of the ylide had reacted. The reaction mixture was then treated with an aqueous alkaline hydrogen peroxide solution. This allows to convert the alkylboron species to the corresponding alcohols. Purification by silica gel chromatography allowed to separate the triphenylarsine oxide formed during the oxidation step and to isolate polymer **3a**−**c**. The yields were generally good (up to 85%).

The formation of the ylide derived from arsonium salt **2d**, which contains a masked oxygenated function, using *tert*-butyllithium as the base, was accompanied by an important degradation. We then employed lithium hexamethyldisilazide (LHMDS), which proved to be more satisfactory. The results obtained in the polymerization of this ylide in the presence of triethylborane are described in Table 1 (entries 10−12). One major difference compared to the previous experiments conducted from alkyl-substituted ylides is that the discoloration of the reaction mixture was much slower in that case, taking 10−30 min, depending on the initial ylide/triethylborane molar ratio. A possible explanation for this behavior is that hexamethyldisilazane derived from the base may form labile adducts with intermediate boron compounds, hence making them less accessible for the ylide.

All polymers were characterized using ^1H and ^{13}C NMR and size exclusion chromatography (SEC). The NMR spectra of polymers **3a**−**d**, which do not contain any asymmetric center, can be easily interpreted. Common characteristic patterns observed for polymers in ^1H NMR are the olefinic proton (triplet), the bis(allylic), methylenic protons (doublet), and the α-hydroxy methylenic protons (singlet). Comparison of the integration of the latter peak with that of peaks belonging to the

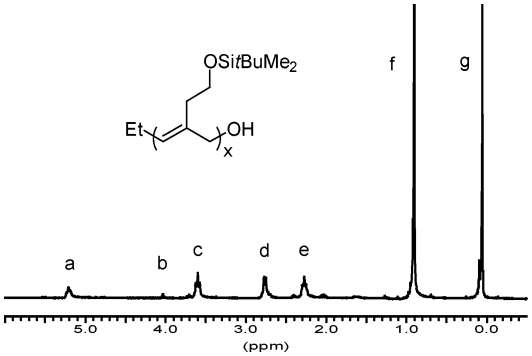
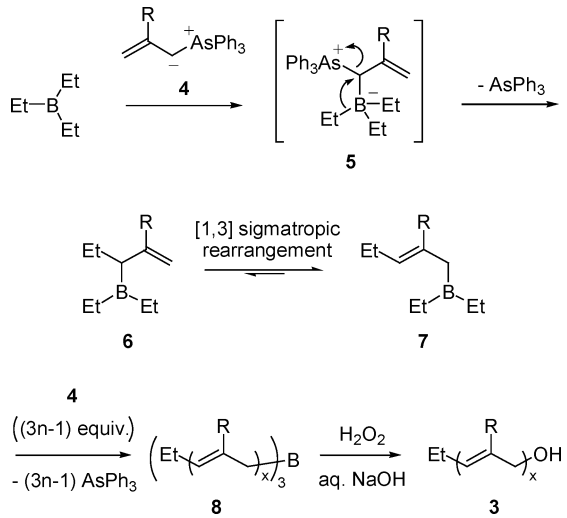


Figure 1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of polymer **3d** (as described in Table 1, entry 12). Spectral assignments of typical protons: (a) ethylenic protons, (b) C*H*$_2$OH, (c) CH_2-OSi, (d) bis(allylic) methylene protons, (e) allylic methylene protons, (f) $(CH_3)_3CSi$, and (g) CH_3Si.

Scheme 4



repetitive unit allowed the determination of the degree of polymerization DP (NMR). A representative ^{1}H NMR spectrum of polymer **3d** is shown in Figure 1.

Sharp peaks corresponding to the carbon atoms of the monomer units are seen in the ^{13}C NMR spectra of polymers **3a**−**d**. Comparison of the ^{13}C NMR chemical shifts observed for polymer **3a** to those reported for the closely related polymers, *cis*-polyisoprene and *trans*-polyisoprene, allowed to attribute the configuration of the double bonds. The reported chemical shifts for the methyl carbon of *trans*-1,4-polyisoprene (δ = 15.76 ppm) and that of *cis*-1,4-polyisoprene (δ = 23.25 ppm) in $CDCl_3$ are significantly different.[9] The chemical shift for the methyl carbon of polymer **3a** (δ = 16.2 ppm) indicates that the double bonds are *E*-configurated. It was assumed that the double bonds in polymers **3b**−**d** were also *E*-configurated. This was also supported by good agreement between the ^{13}C NMR calculated and observed chemical shifts values.

The formation of poly(2-substituted-1-propenylene)s **3a**−**d** may be explained as described in Scheme 4. In the first step, ylide **4** reacts with triethylborane to form an ate complex **5**. This adduct undergoes a rearrangement that involves a 1,2-migration of an ethyl group and concomitant ejection of a triphenylarsine molecule, leading to allylic borane **6**. The latter is then readily converted to isomeric allylic borane **7**, owing to a [1,3] sigmatropic rearrangement. Another molecule of ylide **4** can then react with **7**, allowing the second step of

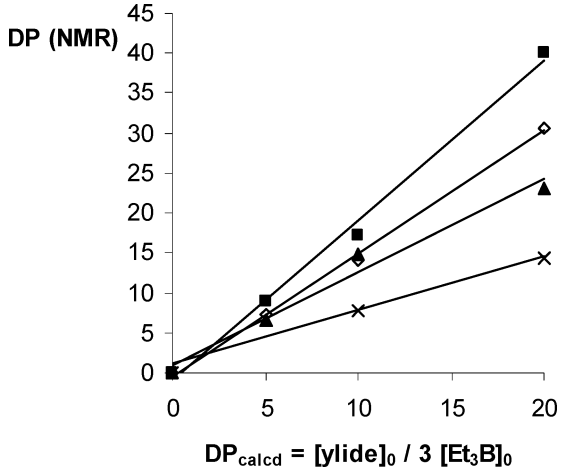


Figure 2. Observed DP of polymers **3a**−**d** (by NMR) vs DP_{calcd} (initial ratio of ylide concentration to 3 × triethylborane concentration): **3a** (open rhomb), **3b** (solid square), **3c** (solid triangle), **3d** (cross).

polymerization to proceed. This sequence of events then proceeds in an analogous manner along the three substituents on the boron atom, as long as ylide **4** is available in the reaction mixture. A polymeric boron compound **8** is eventually obtained. The vanishing of the red color of the solution, due to the ylide, means that the polymerization process is ended. Treatment of the discolored solution with alkaline hydrogen peroxide then affords polymeric alcohol **3**.

It should be pointed out that the [1,3] sigmatropic rearrangement of allylic borane **6** to **7** is highly favored because in the latter compound, the boron atom is in a much less hindered position and the double bond is in a more stabilized position. The same reasoning holds for the [1,3] sigmatropic rearrangements that occur in the next cycles of the polymerization. This property of allylic boron compounds has been studied.[10] The [1,3] sigmatropic rearrangement, which involves an interaction between the double bond and the vacant orbital on the boron atom, has been observed in several allylic organoboranes, which are strong Lewis acids. For example, it was concluded from ^{1}H NMR studies that tris(methallyl)borane rearranged permanently at room temperature.[11]

In each experiment, the actual degree of polymerization was determined from the ^{1}H NMR spectrum as well as from SEC (Table 1). A few discrepancies between DP values obtained either from ^{1}H NMR or from SEC were noted, especially for polymers having low M_n values, for which the detection (two-angle laser light scattering coupled with refractive index detector) becomes less accurate. It is noteworthy that the actual DP of the polymers (obtained from ^{1}H NMR) increases linearly with the DP calculated from the initial ylide/triethylborane molar ratio, which gives credit to a controlled polymerization process (Figure 2).

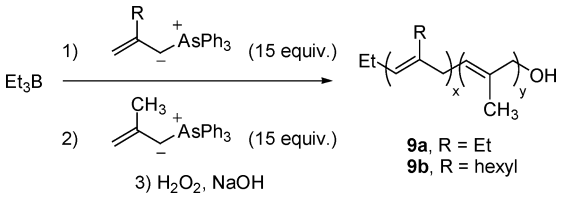
The polydispersity indices (PDI) were in the range 1.2−1.6. Higher PDI were observed for polymers derived from the arsonium salts **4c** and **4d** bearing more bulky groups, when using an initial ylide/triethylborane molar ratio of 60 (Table 1, entries 9 and 12). In general, the actual DP was larger than the calculated DP (determined on the basis of the quantities of reagents, assuming that the polymerization can occur along the three substituents on the boron atom). This suggests that the initiation of the polymerization was not com-

Table 2. Preparation of Block Copolymers 9a and 9b from Triethylborane by Successive Additions of the Ylide Derived from Either 2b or 2c and the Ylide Derived from 2a

entry	R	product	DP_{calcd}[a]	DP[b] (NMR)	DP[c] (SEC)	M_n[c] (SEC)	PDI[c] (SEC)	yield[d] (%)
1	hexyl	**9b**	10	16.9	11.3	1055	1.48	85
2	Et	**9a**	10	11.9	10.3	676	1.72	72

[a] DP calculated from the molar ratio of ylides to triethylborane [= (15+15)/3]. [b] DP determined from ^{1}H NMR spectra integrations. [c] DP, M_n, and PDI determined from SEC. [d] Yield of chromatographed polymer.

Scheme 5



pletely efficient. This could be due to the lower migration aptitude of the ethyl group compared with allylic groups. The rates of 1,2-migration of the three ethyl groups in ate complex **5** are equivalent. Similarly, the migration rates of the three allylic groups in an ate complex derived from a triallylic borane such as **8** should be equivalent. However, the rates of migration of the ethyl and the allylic substituents in an ate complex derived from a boron compound substituted either by two ethyl and one allylic groups (such as **7**) or by one ethyl and two allylic groups are likely to be different. Hence, the polymerization would not proceed exactly in the same manner along the three substituents of the triorganoborane. It cannot be ruled out that the polymerization actually does not occur along one of the three substituents on the boron atom, thus explaining that the observed DP is larger than expected.

Preparation of Block Copolymers from Two Different Ylides. Having shown that several 2-substituted allylic arsonium ylides polymerize to afford poly(2-substituted-1-propenylene)s in the presence of a trialkylborane, we then briefly investigated the possibility to gain access to block copolymers derived from two different ylides that would react successively with the boron species (Scheme 5).

One necessary requirement, to avoid the formation of a random copolymer, is that all of the first ylide monomer has been completely consumed before the addition of the second ylide monomer. As mentioned before, the consumption of the first ylide monomer is simply deduced from the disappearing of the bright red color of the reaction mixture. The results are summarized in Table 2.

For the preparation of copolymer **9b** (entry 1), two solutions of the ylides derived from **2a** and **2c** were prepared. Triethylborane was added at 0 °C to the solution of the ylide derived from **2c**. The discoloration occurred instantaneously, indicating that the ylide monomer was completely consumed. Following the discoloration, the red solution of ylide derived from **2a** was added immediately.[12] The reaction mixture rapidly discolored, indicating that the second ylide monomer was reacting. After usual oxidative treatment and purification, the ^{1}H NMR spectrum displayed the expected signals corresponding to the methyl and hexyl groups arising from the two ylide monomers (Figure 3), clearly indicating that block copolymer **9b** had been formed. The SEC of the polymer obtained from this experiment was indicative of a monomodal distribution (Figure 4).

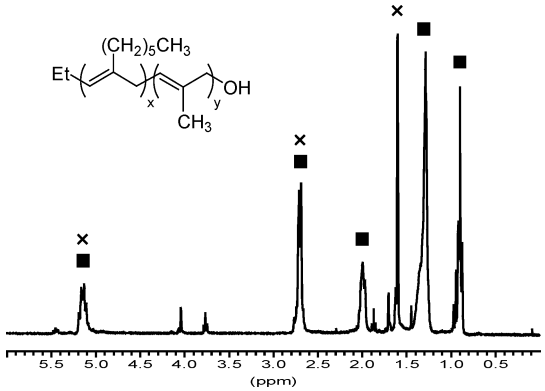


Figure 3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of copolymer **9b** (R = hexyl; as described in Table 2, entry 1). Tags indicate the signals pertaining to **2c**-derived monomer (solid square) or to **2a**-derived monomer (cross).

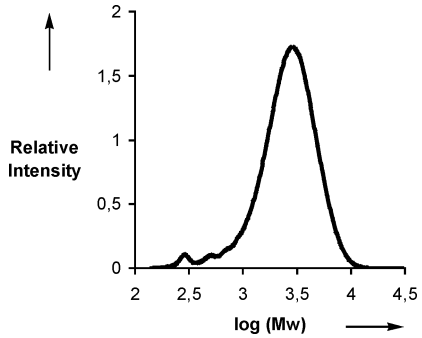


Figure 4. SEC trace for block copolymer **9b**.

Under similar conditions, copolymer **9a** was obtained from successive additions of ylides derived from **2b** and from **2a** (entry 2). Using this method, **9a** and **9b** having a PDI of 1.48 and 1.71, respectively, were thus obtained with good yields.

The following experiment was conducted in order to prove that the polymerization had effectively led to block copolymers and not to random copolymers. Polymer **9b** was thus prepared as described above. An aliquot of the reaction mixture was taken just after the discoloration of the solution containing the first ylide and before the addition of the second ylide derived from **2a**. The reaction was then allowed to proceed to completion. Then both the aliquot and the reaction mixture were oxidized and purified as previously, leading to samples **A** and **B**, respectively. On the basis of the NMR spectra and of the SEC analysis of both samples, it was shown that sample **A** corresponded to polymer **3c**, DP(NMR) = 6.2, and that sample **B** corresponded to polymer **9b**, DP(NMR) = 10.4. This result is in strong support of the formation of a block copolymer rather than a random copolymer. Another evidence of the presence of the block copolymer structure has been obtained from DSC (differential scanning calorimetry) measurements. The copolymer **9b** has been analyzed and showed two distinct T_g (glass transition temperature) at −72 and

−11 °C. These values are very close to the corresponding homopolymers **3a** and **3c**, which gave respectively T_g at −70 and −13 °C.

Conclusion

In conclusion, various linear poly(2-substituted-1-propenylene)s, including one substituted by pendant oxygenated groups, were prepared by reaction of 2-substituted allylic arsonium ylides with a triethylborane. Block copolymers were also obtained from successive additions of different ylides. This paves the way to new polymeric materials.

Experimental Section

Materials. THF was freshly distilled from sodium benzophenone ketyl. Methallyl bromide (**1a**) is commercially available. 2-Bromomethyl-1-butene (**1b**) and 2-chloromethyl-1-octene (**1c**) were prepared by halogenation of the corresponding alcohols. Chloride **1d** was prepared from dimethyl itaconate as previously reported.[13] Reactions were performed under an argon atmosphere. TLC: silica gel $60F_{254}$ plates (Merck), with detection by UV light and with an ethanol solution of phosphomolybdic acid. Column chromatography: 40−63 μm Merck silica gel. IR: Perkin-Elmer 2000. Melting points (uncorrected): Büchi 535. NMR: Bruker AM 300 (300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively). $CDCl_3$ was used as solvent; chemical shifts (δ) are in ppm (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad); coupling constants (J) are in Hz.

Characterization. Number-averaged molecular weights (M_n), weight-averaged molecular weights (M_w), and polydispersity indices (PDI = M_w/M_n) were determined using steric exclusion chromatography (SEC) in THF at 30 °C and a flow rate of 1 mL min^{-1}. Two 7.5 mm diameter × 300 mm Polymer Labs 3 μm particle diameter mixed-E PLgel columns were connected in line to a Shimadzu LC-10AD pump, a degasser (Erma, ERC-3312), a Shimadzu RID-6A differential refractive index (DRI) detector, and a PD 2000 (Precision Detectors, Inc.) two-angle light scattering (TALLS) detector. The static measurements were done at both 15° and 90° and simultaneously coupled to a dynamic light scattering analysis. The reported M_n and M_w are absolute values; they were obtained from the measurements at 90°. Differential scanning calorimetry (DSC) was performed on a TA Instrument DSC 2920, at a scan rate of 10 °C min^{-1} from −100 to 100 °C.

I. Preparation of Arsonium Tetrafluoroborate Salts 2b−d. Typical Preparation: 1-(2-Methyleneoctyl)triphenylarsonium Tetrafluoroborate (2c). A 30 mL heavy-walled glass tube was charged in a nitrogen-flushed glovebox with 2-chloromethyl-1-octene (1.55 g, 19.31 mmol), anhydrous sodium iodide (1.45 g, 19.31 mmol), triphenylarsine (4.43 g, 28.97 mmol), and acetonitrile (20 mL). The screwed tube was wrapped in an aluminum foil in order to protect its contents from the light and then heated at 40 °C under stirring for 4 days. The reaction mixture was concentrated under vacuum. The brown residue was dissolved in dichloromethane (50 mL). The organic phase was washed with 10% aqueous sodium thiosulfate solution. To the pale yellow organic phase was then added an aqueous solution of $NaBF_4$ (105 g, 100 equiv in 125 mL of water), and the mixture was vigorously stirred for 2 h. The aqueous phase was then extracted with dichloromethane (3 × 40 mL). The combined organic phases were dried over $MgSO_4$ and then concentrated under vacuum. The residue was triturated in a 1:1 ether/pentane mixture. A broken white solid precipitates. The broken white solid obtained was filtered on a sintered glass and dried in a desiccator. Recrystallization from AcOEt afforded 2.305 g (46%) of arsonium salt **2c** as white crystals: mp = 132.5−133.7 °C. IR (KBr pellet) ν_{max} = 3062, 2958, 2926, 2857, 2661, 2165, 2010, 1908, 1827, 1641, 1581, 1484, 1464, 1441, 1405, 1341, 1316, 1284, 1218, 1189, 1061, 997, 924, 747, 691, 520, 465 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79−7.65 (m, 15H), 5.08 (bs, 2H), 4.19 (s, 2H), 1.76 (t, J = 7.6 Hz, 2H), 1.26−1.07 (m, 8H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.4, 134.3, 132.9, 132.7, 121.4, 119.6, 36.9, 33.1, 31.5, 28.6, 27.0, 22.5, 14.1. Anal. Calcd for $C_{27}H_{32}AsBF_4$: C, 62.57; H, 6.22. Found: C, 62.54; H, 6.08.

1-(Methallyl)triphenylarsonium Tetrafluoroborate (2a). Compound **2a** was prepared from methallyl bromide (4.83 g, 47.92 mmol) following the general procedure, except that no sodium iodide was employed, the tube was heated at 90 °C for 2 days, and 30 equiv of $NaBF_4$ was used. After precipitation of the crude product by addition of ether, filtration, and drying over P_2O_5, arsonium salt **2a** (9.44 g, 44%) was obtained as a white solid, which need not further purification: mp = 184.8−186.9 °C. IR (thin film, KBr pellet) ν_{max} = 3159, 3062, 2986, 2931, 2659, 2357, 2163, 1976, 1897, 1823, 1768, 1645, 1581, 1483, 1439, 1386, 1338, 1314, 1287, 1188, 1081, 920, 861, 816, 737, 688, 519 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.89−7.73 (m, 15H), 5.16 (s, 1H), 5.07 (s, 1H), 4.38 (s, 2H), 1.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 135.4, 134.1, 131.9, 123.0, 121.4, 34.5, 24.1. Anal. Calcd for $C_{22}H_{22}AsBF_4$: C, 58.96; H, 4.95. Found: C, 58.84; H, 5.07.

1-(2-Methylenebutyl)triphenylarsonium Tetrafluoroborate (2b). Following the general procedure, arsonium salt **2b** was prepared from 2-bromomethyl-1-butene (2.468 g, 16.56 mmol). Recrystallization (7:3 AcOEt/THF mixture) afforded 4.529 g (59%) of compound **2b** as a white solid: mp = 141.4−143.0 °C. IR (KBr pellet) ν_{max} = 3399, 3058, 2978, 2912, 2660, 2163, 1997, 1825, 1639, 1580, 1481, 1439, 1402, 1317, 1286, 1189, 1062, 919, 856, 742, 687, 524, 466 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79−7.63 (m, 15H), 5.07 (s, 1H), 5.06 (s, 1H), 4.20 (s, 2H), 1.84 (q, J = 7.3 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 138.8, 134.4, 132.8, 131.0, 121.2, 118.5, 33.1, 29.9, 11.5. Anal. Calcd for $C_{23}H_{24}AsBF_4$: C, 59.77; H, 5.23. Found: C, 59.69; H, 5.25.

1-[2-Methylene-4-(*tert*-butyldimethylsilyloxy)butyl]-triphenylarsonium Tetrafluoroborate (2d). Following the general procedure, arsonium salt **2d** was prepared from 2-chloromethyl-4-(*tert*-butyldimethylsilyloxy)-1-butene (2.097 g, 8.94 mmol). Silica gel chromatography (95:5 CH_2Cl_2/MeOH) afforded 3.234 g (61%) of compound **2d** as a white solid: mp = 118.8−120.3 °C. IR (KBr pellet) ν_{max} = 3407, 3053, 2955, 2930, 2859, 1833, 1641, 1579, 1475, 1439, 1362, 1255, 1189, 1085, 1001, 930, 835, 776, 746, 690, 522, 469 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79−7.64 (m, 15H), 5.17 (s, 1H), 5.12 (s, 1H), 4.29 (s, 2H), 3.67 (t, J = 5.8 Hz, 2H), 2.03 (t, J = 6.1 Hz, 2H), 0.83 (s, 9H), −0.04 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 135.2, 134.4, 132.9, 131.0, 121.5, 121.2, 61.8, 39.7, 33.4, 26.0, 18.3, −5.4. Anal. Calcd for $C_{29}H_{38}AsBF_4OSi$: C, 58.79; H, 6.47. Found: C, 58.75; H, 6.31.

II. Preparation of Homopolymers 3a−d. Typical Polymerization Procedure: Polymer 3a. To a suspension of arsonium salt **2a** (0.396 g, 0.884 mmol) in anhydrous THF (10 mL) cooled to −78 °C was added dropwise a 1.7 M solution of *tert*-butyllithium in pentane (0.520 mL, 0.884 mmol). A yellow persisting coloring appeared as soon as the first drop was introduced. By the end of the addition, the medium was bright red and quasi-limpid. Stirring was continued for 40 min at −78 °C and then for 5 min at 0 °C. A 1 M solution of triethylborane in hexane (59 μL, 0.059 mmol) was added at once. An instantaneous discoloration of the solution occurred. The pale yellow solution was stirred for 1 h at 0 °C, and then a previously combined mixture of 30% aqueous hydrogen peroxide (5 mL) and of 15% aqueous sodium hydroxide (5 mL) was added cautiously. The reaction mixture was then vigorously stirred overnight at room temperature. An aqueous saturated NH_4Cl solution (40 mL) was added. The aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic phases were dried over $MgSO_4$ and then concentrated under vacuum. Silica gel chromatography (pentane, then 6:4 pentane/AcOEt) afforded polymer **3a** as a colorless oil (0.044 g, 79%). Degree of polymerization according to the NMR spectrum: 7.3; according to SEC: 10.2 (see Table 1, entry 1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.45 (t, J = 7.3 Hz, 1H); 5.17 (t, J = 7.3 Hz, 6.5H); 4.04 (s, 2H); 2.70 (d, J = 6.7 Hz, 14H); 2.01 (m, 2H); 1.70 (bs, 1H, OH); 1.60 (s, 19.5H); 0.95 (t, J = 7.6 Hz, 3H).

The ^{13}C NMR spectrum of a polymer **3a** having a larger degree of polymerization (see Table 1, entry 3) was recorded: ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 135.8, 122.4, 38.3, 16.2.

Polymer 3b. Following the general procedure, polymerization of arsonium salt **2b** (0.388 g, 0.84 mmol) in the presence of triethylborane (15:1 arsonium salt/triethylborane ratio) afforded, after purification by chromatography (pentane and then 6:4 pentane/AcOEt), polymer **3b** as a colorless oil (0.050 g, 83%). Degree of polymerization according to the NMR spectrum: 9; according to SEC: 13.1 (see Table 1, entry 4). ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.42 (t, J = 7.3 Hz, 1H), 5.12 (t, J = 7.3 Hz, 8.2H), 4.08 (s, 2H), 2.72 (d, J = 7.9 Hz, 18.4H), 2.15 (q, J = 7.5 Hz, 2H), 2.03 (m, 21.2H), 0.97 (bt, J = 7.9 Hz, 33.1H).

The ^{13}C NMR spectrum of a polymer **3b** having a larger degree of polymerization (see Table 1, entry 6) was recorded: ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 141.5, 122.3, 34.9, 23.3, 13.2.

Polymer 3c. Following the general procedure, polymerization of arsonium salt **2c** (0.41 g, 0.79 mmol) in the presence of triethylborane (15:1 arsonium salt/triethylborane ratio) afforded, after purification by chromatography (pentane and then 6:4 pentane/AcOEt), polymer **3b** as a colorless oil (0.065 g, 62%). Degree of polymerization according to the NMR spectrum: 6.5; according to SEC: 8.1 (see Table 1, entry 7). ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.43 (t, J = 6.7 Hz, 1H), 5.13 (bt, J = 6.7 Hz, 6.0H), 4.06 (s, 2H), 2.71 (d, J = 7.3 Hz, 13.0H), 2.09 (q, J = 7.6 Hz, 2H), 2.00 (m, 16.5H), 1.56 (bs, 1H, OH), 1.29 (m, 68.5H), 0.94 (t, J = 7.9 Hz, 3H), 0.90 (t, J = 6.4 Hz, 24.2H).

The ^{13}C NMR spectrum of a polymer **3c** having a larger degree of polymerization (see Table 1, entry 9) was recorded: ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 140.1, 123.1, 35.6, 32.0, 30.3, 29.7, 28.5, 22.8, 14.2.

Polymer 3d. Following the general procedure, except that lithium hexamethyldisilazide (1 M in THF) was employed as the base, polymerization of arsonium salt **2d** (0.444 g, 0.75 mmol) in the presence of triethylborane (15:1 arsonium salt/triethylborane ratio) afforded, after purification by chromatography (pentane and then 8:2 pentane/ethyl acetate), polymer **3d** as a colorless oil (0.101 g, 65%). Degree of polymerization according to the NMR spectrum: 6.5; according to SEC: 5.1 (see Table 1, entry 10). ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.51 (t, J = 6.7 Hz, 1H), 5.18 (bt, J = 7.6 Hz, 5.5H), 4.03 (s, 2H), 3.71 (t, J = 6.1 Hz, 2H) 3.60 (bt, J = 7.3 Hz, 11.9H), 2.75 (bd, J = 6.7 Hz, 11.6H), 2.40 (t, J = 5.8 Hz, 2H), 2.27 (bt, J = 6.7 Hz, 11.1H), 2.03 (m, 2H), 1.63 (bs, 1H, OH), 0.95 (t, J = 7.9 Hz, 3H), 0.90 (s, 66.1H), 0.10 (s, 6H), 0.06 (s, 34.9H).

The ^{13}C NMR spectrum of a polymer **3d** having a larger degree of polymerization (see Table 1, entry 12) was recorded: ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 136.5, 125.2, 62.2, 36.7, 34.3, 26.1, 18.4, −5.1.

III. Preparation of Copolymers 9a,b. Typical Copolymerization Procedure: Polymer 9b. Two arsonium ylides were prepared respectively from 2-(methylene)octyltriphenylarsonium tetrafluoroborate **2c** (0.619 g, 1.195 mmol) and methallyltriphenylarsonium tetrafluoroborate **2a** (0.539 g, 1.195 mmol) in two different flasks, as described in the typical polymerization. The solution of methallyl ylide was withdrawn into a syringe under argon. The syringe needle was inserted through the septum of the flask containing the solution of ylide derived from **2c**. A 1 M solution of triethylborane in hexane (80 μL, 0.080 mmol) was added at once to this flask at 0 °C. An instantaneous discoloration occurred. Immediately after discoloration, the red solution of methallyl ylide was quickly added at once. At the beginning of the addition, the solution color faded as soon as it reached the reaction mixture. With the end of addition the discoloration became a little slower. Stirring was continued during 1 h at 0 °C, and then a previously combined mixture of 30% hydrogen peroxide (5 mL) and of 15% sodium hydroxide (5 mL) was added cautiously. The reaction mixture was then vigorously stirred overnight at room temperature. An aqueous saturated NH_4Cl solution (40 mL) was added. The aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic phases were dried over $MgSO_4$ and then concentrated under vacuum. Silica gel chromatography (pentane, then 6:4 pentane/AcOEt) afforded polymer **9b** as a pale yellow oil (190 mg, 85%). Degree of polymerization according to the NMR spectrum: 16.5; according to SEC: 11.3 (see Table 2, entry 2). ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.43 (t, J = 6.1 Hz, 1H), 5.19−5.11 (m, 16.1H), 4.04 (s, 2H), 2.69 (d, J = 6.7 Hz, 34.0H), 2.00 (m, 19.5H), 1.70 (s, 1H, OH), 1.60 (s, 23.7H), 1.29 (m, 78.8H), 0.95 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 6.7 Hz, 28.4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (major peaks) = 140.1, 135.9, 123.1, 122.4, 69.0, 38.3, 35.6, 31.9, 30.4, 29.7, 28.5, 22.8, 21.1, 16.2, 14.7, 14.2. δ (minor peaks) = 126.6, 37.9, 35.3.

Polymer 9a. Following the general procedure, copolymerization using first the ylide derived from **2b** (0.308 g) and then the ylide derived from **2a** (0.299 g) in the presence of triethylborane (15:15:1 **2b/2a**/triethylborane ratio) afforded, after purification by chromatography, polymer **9a** as a colorless, viscous oil (63.3 mg, 72%). Degree of polymerization according to the NMR spectrum: 11.9; according to SEC: 10.3 (see Table 2, entry 3). ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.42 (t, J = 8.2 Hz, 1H), 5.19−5.09 (m, 11.2H), 4.08 and 4.03 (s, 2H), 2.71 (m, 24.5H), 2.03 (q, J = 7.1 Hz, 17.9H), 1.70 (s, 3H), 1.60 (s, 14.8H, OH), 0.97 (bt, J = 7.3 Hz, 25.9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (major peaks) 141.5, 135.9, 122.4, 66.9, 38.3, 34.9, 23.3, 21.0, 16.2, 14.8, 13.1. δ (minor peaks) = 140.0, 126.1, 37.9, 35.3, 21.0, 13.3.

Acknowledgment. We thank France Costa-Torro (LCM, CNRS/Université Pierre et Marie Curie) for the thermogravimetric analysis.

References and Notes

(1) (a) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747−3792. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(2) (a) Lee, M.; Cho, B.-K.; Zin, W.-C. *Chem. Rev.* **2001**, *101*, 3869−3892. (b) Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204*, 265−273. (c) Förster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688−714.
(3) Bawn, C. E. H.; Ledwith, A. *Prog. Boron Chem.* **1964**, *1*, 345−368 and references therein.
(4) (a) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049−9050. (b) Shea, K. J. *Chem.—Eur. J.* **2000**, *6*, 1113−1119 and references therein. (c) Zhou, X.-Z.; Shea, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 11515−11516.
(5) Goddard, J.-P.; Lixon, P.; Le Gall, T.; Mioskowski, C. *J. Am. Chem. Soc.* **2003**, *125*, 9242−9243.
(6) Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1981**, *103*, 1283−1285.
(7) For reviews on arsonium ylides chemistry, see: (a) Smith, M. D. In *Science of Synthesis*; Fleming, I., Ed.; Georg Thieme Verlag: Stuttgart, 2002; Vol. 4, pp 13−51. (b) Lloyd, D.; Gosney, I.; Ormiston, R. A. *Chem. Soc. Rev.* **1987**, *16*, 45−74.
(8) Another sample of polymer **3a** has previously been prepared by this method (see ref 5) but was not characterized using size exclusion chromatography (SEC) at that time.
(9) Sato, H.; Ono, A.; Tanaka, Y. *Polymer* **1977**, *18*, 580−586.
(10) Mikhailov, B. M. *Organomet. Chem. Rev. A* **1972**, *8*, 1−65.
(11) The activation energy for the rearrangement of tris(methallyl)borane is 9.8 kcal mol^{-1}: Bogdanov, V. S.; Bubnov, Y. N.; Bochkareva, M. N.; Mikhailov, B. M. *Dokl. Akad. Nauk SSSR*, *Ser. Khim.* **1971**, *201*, 605−608; *Chem. Abstr. 78*, 28965.
(12) In another experiment, the second ylide was added 5 min after the discoloration of the reaction mixture. In that case, the SEC pattern of the isolated polymer **9b** showed a bimodal distribution. Thus, it is highly preferable to add the second ylide as soon as the first discoloration occurred.
(13) Hughes, R. C.; Dvorak, C. A.; Meyers, A. I. *J. Org. Chem.* **2001**, *66*, 5545−5551.

MA047693E