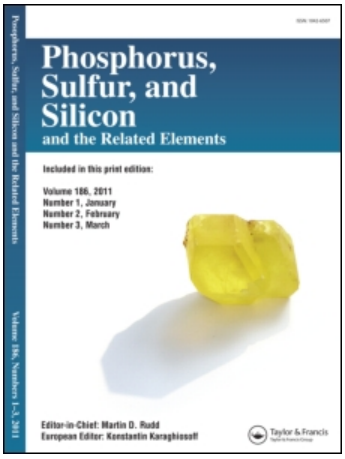

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF NEW PHOSPHONATED MONOMERS

Bérengère Rixens[a]; Gilles Boutevin[a]; Ahmed Boulahna[a]; Yves Hervaud[a]; Bernard Boutevin[a]
[a] Laboratoire de Chimie Macromoléculaire, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, France

Online publication date: 16 August 2010

To cite this Article Rixens, Bérengère , Boutevin, Gilles , Boulahna, Ahmed , Hervaud, Yves and Boutevin, Bernard(2004) 'SYNTHESIS OF NEW PHOSPHONATED MONOMERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 12, 2617 — 2626
To link to this Article: DOI: 10.1080/10426500490494723
URL: http://dx.doi.org/10.1080/10426500490494723

Phosphorus, Sulfur, and Silicon, 179:2617–2626, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490494723

Taylor & Francis
Taylor & Francis Group

SYNTHESIS OF NEW PHOSPHONATED MONOMERS

Bérengère Rixens, Gilles Boutevin, Ahmed Boulahna, Yves Hervaud, and Bernard Boutevin
Laboratoire de Chimie Macromoléculaire, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, France

(Received May 11, 2004; accepted June 1, 2004)

Two phosphonated methacrylates containing urethane group were synthesized by reacting the isocyanatoethyl methacrylate (IEM; CH_2=$C(CH_3)COO(CH_2)_2NCO$) and a phosphonated alcohol ($(OH(CH_2)_xP(O)(OMe)_2$, x = 1 or 2), and they are hydrolyzed into mono- and diacid monomers. All these products were characterized in ^1H and ^{31}P NMR. Unlike usual methods (esterification and transesterification), these syntheses were quantitative and easy to realize.

Keywords: Hydrolysis; isocyanatoethyl methacrylate; phosphonated alcohols; phosphonated monomers

INTRODUCTION

Phosphonated monomers and polymers are of interest in a variety of applications, including flame-retardant, anticorrosive, and adhesion. Indeed, the stability toward hydrolysis of phosphonated polymers is better than that of phosphated polymers because P–C bonds are preferred. Some phosphonated monomers, such as CH_2=$C(R_1)COO(CH_2)_nP(O)(OR_2)_2$ with R_1 = H or CH_3,[1,2] CH_2=$C(CH_3)COO\ CH_2CHOHCH_2\ P(O)(OR_2)_2$,[3] or carbamoyl phosphonates obtained by reaction between an isocyanate and a dialkyl phosphite,[4–6] have been described previously.

The aim of this study is to synthesize new polymerizable monomers bearing phosphonated functions, and to decrease the synthesis steps and to increase the yield. A direct reaction of a methacrylate isocyanate with a phosphonated alcohol is described in this article.

Address correspondence to Bernard Boutevin, Ecole Nationale Supérieure, Heterochimie Mol. et Macromol, 8, rue de l'Ecole Normale, Montpellier, Cedex 5 F-34296, France. E-mail: boutevin@cit.enscm.fr

RESULTS AND DISCUSSION

Our aim is to synthesize new phosphonated monomers by reaction between an isocyanate group and an alcohol group. This type of reaction, widely described in the literature, can be catalyzed by tertiary amine or organic metallic compounds such as dibutyl tin dilaurate (DBTDL)[7–10] or SmI_2.[11] This reaction can be also realized without catalyst and with[12–15] or without solvent.[16,17] We decided to work with an isocyanate bearing a methacrylate function, i.e., isocyanatoethyl methacrylate (IEM). Reacting IEM with a dialkyl phosphite led to a monomer with the following structure: $CH_2{=}C(CH_3)COO\text{-}(CH_2)_2\text{-}NH{-}CO{-}P(O)(OR)_2$ (R=Me, Et).[5] Some earlier papers described the reaction between IEM and sugar[18] or hydroxyethyl methacrylate,[10] thus the reaction with this isocyanate and a phosphonated alcohol was studied. Moreover the addition of hydroxyphosphonate to phenyl thiocyanate[19,20] can be realized without catalyst with acrylonitrile as solvent. So, according to these papers we chose to synthesize the monomers without catalyst and with or without solvent.

For the first time, the synthesis of two phosphonated alcohols, with one or two carbon spacer, is described. Then reactions with the methacrylate are studied.

Synthesis of Phosphonated Precursors

Synthesis of Dimethyl Hydroxymethylphopsphonate Alcohol in C1

Recent papers from our laboratory described this alcohol synthesis.[21] Thus it was achieved as already described[21,22] via a Pudovik[23] reaction using dimethyl hydrogenophosphonate ($HPO(OCH_3)_2$), paraformaldehyde, and anhydrous potassium carbonate as catalyst.

Synthesis of Dimethyl 2-Acetoxyethylphosphonate: Alcohol in C2

The literature described this alcohol synthesis in two steps: a telomerization of vinyl acetate with dialkyl hydrogenophosphonate as transfer agent.[24–26] followed by an acetate function cleavage.[27] Recent works realized by our group[22,28] allowed the optimization of this reaction.

Monomer Synthesis

The phosphonated monomers were always synthesized with reagents in stoichiometric conditions. This synthesis can be realized with or without

solvent, leading in both cases to a quantitative yield. Two syntheses are described in this article: the first one with solvent with C1 alcohol and the second one without solvent with C2 alcohol. These monomers were then hydrolysed, leading to mono- and diacid compounds.

Monomer Synthesis with C1 Alcohol in Solvent

To avoid the urea formation, the mixture had to be completely dehydrated before reaction between IEM and an alcohol.

An azeotropic evaporation was realized during 30 min (70°C/160 mm Hg) to eliminate the water contained in phosphonated alcohol. Then IEM was added drop by drop under inert atmosphere. The reaction time was 10 h at room temperature, and the monomer was obtained with quantitative yield (Figure 1).

This reaction was analyzed by infrared spectroscopy. The NCO ($\nu = 2160\ cm^{-1}$) and OH ($\nu = 3450\ cm^{-1}$) bands totally disappeared and two new bands at 1730 cm^{-1} and 3200 cm^{-1} appeared, respectively characterizing a carbonyl and NH urethane functions, proving a quantitative reaction.

The ^1H NMR spectrum (Figure 2) showed two doublets at 3.6 ppm and 4.3 ppm, respectively corresponding to phosphonic ester ($PO(OC\mathbf{H}_3)_2$) and CH_2 in the α position of the phosphonated group. It also characterized the methacrylic protons, the NH urethane group, and the methacrylic methyl. The ^{31}P NMR spectrum proved the quantitative reaction. Indeed, the alcohol signal at 26 ppm totally disappeared and a singlet appeared at 23 ppm, corresponding to the monomer.

Monomer Synthesis with C2 Alcohol

This reaction was performed without solvent. Phosphonated alcohol and IEM were introduced under inert atmosphere in stoichiometric conditions. After 6 h of reaction, the monomer was obtained with quantitative yield (Figure 3).

The phosphonated monomer (IEMPC2) was characterized by ^1H and ^{31}P NMR spectroscopy. The ^1H NMR (Figure 4) showed a doublet corresponding to phosphonic esters, a doublet of triplet for methylene in α position of phosphonated group, and the triplet of NH. The characteristic methacrylic protons appeared as two singlets and the methacrylic

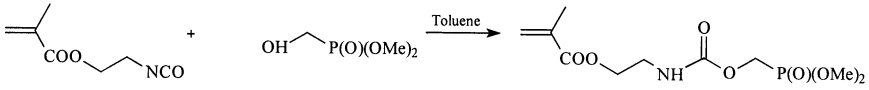

FIGURE 1 Synthesis of phosphonated monomer IEMPC1.

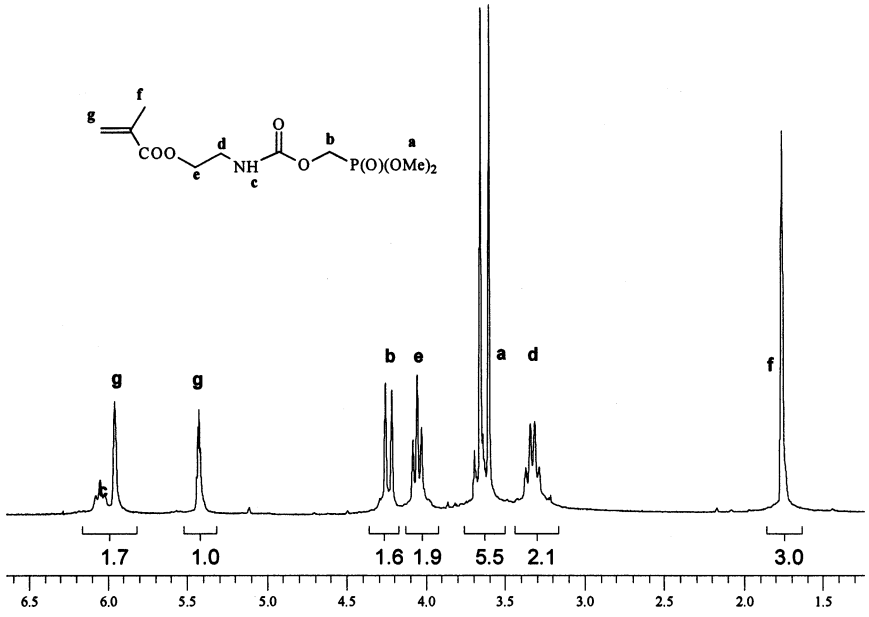

FIGURE 2 ^{1}H NMR spectrum in $CDCl_3$ of IEMPC1.

methyl as a singlet. Moreover, the protons of the phosphonated alcohol signal totally disappeared. The ^{31}P NMR spectrum proved the quantitative reaction: a singlet appeared at 30.4 ppm, corresponding to the monomer.

The reaction rate was followed by ^{31}P NMR. The reaction was complete after 6 h. The results are summarised in Table I. Figure 5 shows the monomer formation versus time. The reaction was fast at the beginning; 68.5% of conversion was obtained after 1 h. Then the reaction slowed down, possibly due to an increase of the viscosity. The reaction was quantitative after 6 h.

Hydrolysis of Phosphonic Ester Functions of Monomers

Two cleavage methods could be used to hydrolyze a phosphonic ester (Figure 6). By using Sodium Iodide a monodealkylation of phosphonic esters[2,29] led to a salt. This salt acidified by an ionic exchange resin,

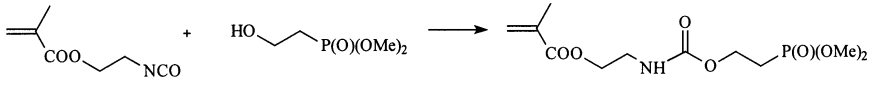

FIGURE 3 Synthesis of phosphonated monomer IEMPC2.

TABLE I Rate Reaction of the IEMPC2 Synthesis

Reaction time (h)	0	1	2	3	4	5	6
% molar of phosphonated alcohol	100	31.5	23.1	17.7	12.3	7.1	2.7
% molar of monomer IEMPC2	0	68.5	76.9	82.3	87.7	92.9	97.3

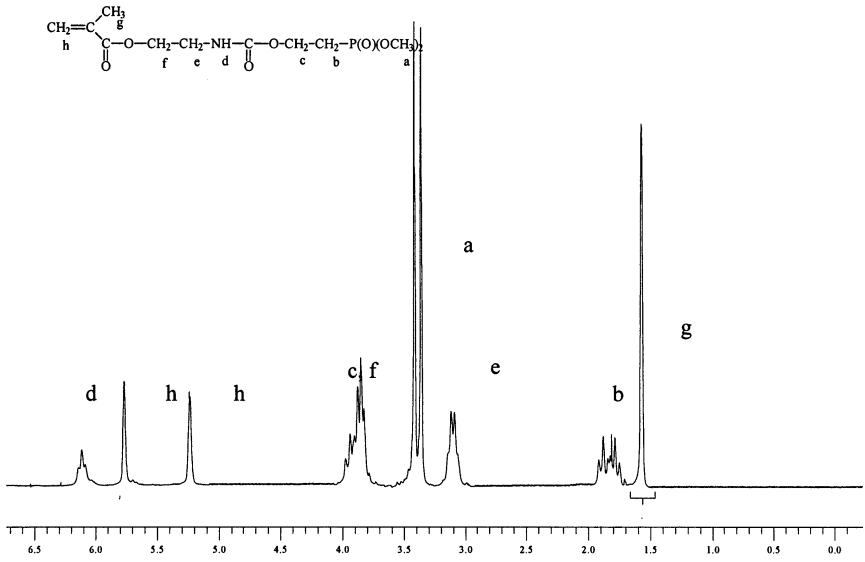

FIGURE 4 ^{1}H NMR spectrum of IEMPC2.

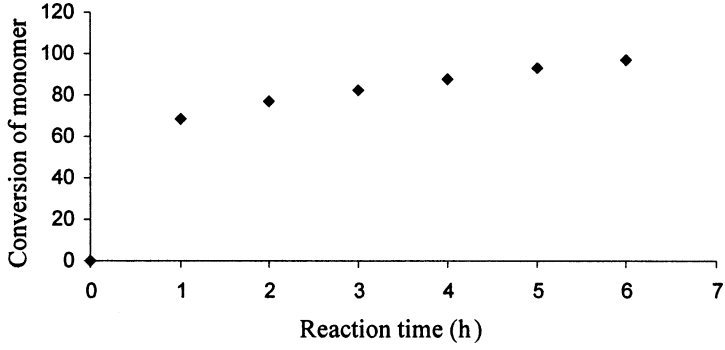

FIGURE 5 Evolution of monomer formation versus time.

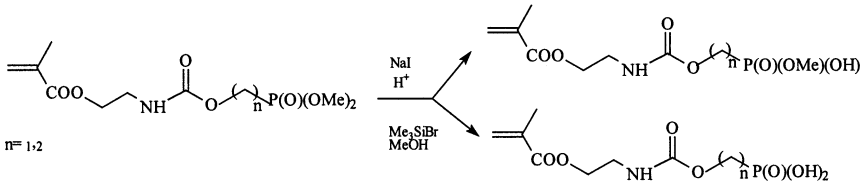

FIGURE 6 Hydrolysis reactions of phosphonic esters.

leading to a monoacid monomer. The diacid monomer was obtained quantitatively by a silylation using bromotrimethyl silane followed by methanolysis.[30–32]

Synthesis of Monoacid Monomer

The monoacid monomer was selectively synthesized by a methanol hydrolysis in two steps in neutral medium. First, a dealkylation reaction with Sodium iodide (at 50°C during 5 h) led to the phosphonated monosalt. Then an acidification reaction was realized in methanol with a sulfonic resin. NMR analysis was carried out. For IEMPC1 the ^{1}H NMR spectrum showed an intensity decrease of the signal at 3.8 ppm for the methylphosphonated groups. The integral value of this signal (6H for the diester form) was equal to 3H, which confirmed the monohydrolysis. On the ^{31}P NMR, the singlet at 21.5 ppm was attributed to the monoacid form. Similar results were obtained with the second monomer IEMPC2.

Synthesis of Diacid Monomer

The diacid monomers were synthesized by silylation of phosphonic esters. This reaction was realized in dichloromethane by addition of bromotrimethylsilane followed by methanolysis. This reaction was performed with both monomers IEMPC1 and IEMPC2. The ^{1}H NMR spectrum showed that the methylphosphononic (dimethyl phosphonate) ($P(O)(OCH_3)_2$) ester signal totally disappeared, proving the diacid monomer structure. The ^{31}P NMR spectrum showed a singlet at 20 ppm for IEMPC1 and a singlet at 26 ppm with IEMPC2.

CONCLUSION

This article reports the synthesis of two phosphonated methacrylate monomers. The mono- and dihydrolysis were realized with both monomers. These products were obtained by reaction between a methacrylate bearing an isocyanate function (IEM) and two phosphonated alcohols with one or two carbon spacer. Unlike the usual

esterification and transesterication techniques, these syntheses were quantitative and easy to achieve.

EXPERIMENTAL

^{1}H and ^{31}P NMR analyses were performed on a 200 MHz Bruker apparatus in $CDCl_3$. The internal reference is tetramethylsilane (TMS) for ^{1}H NMR and orthophosphoric acid H_3PO_4 for ^{31}P NMR. Protons were irradiated for ^{31}P NMR analyses in order to suppress the couplings between phosphorus and hydrogen atoms. Chemical shifts are given in ppm, and the assignations s, d, t, q, and m mean singlet doublet, triplet, quadruplet, and multiplet, respectively.

Synthesis of Phosphonated Precursors

The dimethyl hydroxymethyl phosphonate (alcohol C1) and the dimethyl hydroxyethyl phosphonate (alcohol C2) had been synthesized as already described.[21,22,24–28]

Monomers Synthesis

Synthesis of IEMP with Phosphonated Alcohol (C1): IEMPC1

In a two-necked, round-bottom flask (100 ml) equipped with a Dean-Stark, 9.03 g (6.45×10^{-2} mol.) of phosphonated alcohol (C1) and 50 ml of toluene were introduced. An azeotropic evaporation of water was realized during half an hour (70°C, 160 mm Hg). Then, 10 g (6.45×10^{-2} mol.) of 2-isocyanatoethyl methacrylate (IEM) were added drop by drop in the mixture at room temperature and under inert atmosphere (Ar).

The reaction was monitored by infrared spectroscopy (FTIR). After 10 h at room temperature, the phosphonated monomer was obtained with a quantitative yield.

^{1}**H** NMR ($CDCl_3$) δ (ppm): 1.5 (s, 3H, $CH_2{=}CC\mathbf{H}_3)_2$, 3.3 (q, 2H, $OCH_2C\mathbf{H}_2NH$), 3.4 (d, 6H, $P(OC\mathbf{H}_3)_2$), 4 (t, 2H, $OC\mathbf{H}_2CH_2NH$); 4.3 (d, 2H, $C\mathbf{H}_2P(O)(OMe)_2$); 5.5 (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6 (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6.1 (t, 1H, $CH_2N\mathbf{H}$). ^{31}**P** NMR ($CDCl_3$): δ(ppm): 23 (s).

Synthesis of IEMP with Phosphonated Alcohol (C2): IEMPC2

In a round-bottom flask, 10 g (6.45×10^{-2} mol.) of 2-isocyanatoethyl methacrylate (IEM) and 9.93 g (6.45×10^{-2} mol.) of phosphonated

alcohol (C2) were introduced. The reaction was carried out in bulk at room temperature under nitrogen and was quantitative after 6 h. The reaction rate was followed by ^{31}P NMR spectroscopy.

^{1}**H** NMR ($CDCl_3$) δ (ppm): 1.5 (s, 3H, $CH_2{=}CC\mathbf{H}_3)_2$, 1.6–1.9 (m, 2H, $OCH_2C\mathbf{H}_2P$), 3–3.2 (m, 2H, $C\mathbf{H}_2NH$), 3.4 (d, 6H, $P(OC\mathbf{H}_3)_2$), 3.8–4 (m, 4H, $OC\mathbf{H}_2$), 5.5 ppm (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6 ppm (s, H, $C\mathbf{H}_2{=}C(CH_3)$), 6.1 (m, 1H, N**H**) ^{31}**P** NMR ($CDCl_3$) δ (ppm): 30 (s).

Hydrolysis of Phosphonated Functions of Monomers

Synthesis of the Monoacid Product

In a round-bottom flask equipped with a condenser, the phosphonated monomer (C1) (5 g, 1.78×10^{-2} mol.) and sodium iodide (4 g, 2.37×10^{-2} mol.) were introduced in 50 ml of acetone. The mixture was heated at 50°C during 14 h. Then, the solution was cooled at room temperature during 6 h. The phosphonated salt was filtered and washed twice with acetone to eliminate of iodine salts. The obtained powder was dried under vacuum, 70% yield.

The phosphonated salt was dissolved in methanol and treated by 10 g of sulfonic resin (Amberlite IR-120) with chromatographic column. The phosphonic monoacid monomer was obtained after evaporation of methanol (96% yield).

IEMP C1. ^{1}**H** NMR (**$CDCl_3$**) δ (ppm): 1.5 (s, 3H, $CH_2{=}CC\mathbf{H}_3)_2$, 3.3 (q, 2H, $OCH_2C\mathbf{H}_2NH$), 3.4 (d, 3H, $P(OC\mathbf{H}_3)_2$), 4 (t, 2H, $OC\mathbf{H}_2CH_2NH$); 4.3 (d, 2H, $C\mathbf{H}_2P(O)(OCH_3)(OH)$); 5.5 (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6 (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6.1 (t, 1H, $CH_2N\mathbf{H}$). ^{31}**P** NMR (**$CDCl_3$**) δ (ppm): 21.5 (s).

IEMP C2. ^{1}**H** NMR (CD_3OD) δ (ppm): 1.5 (s, 3H, $CH_2{=}CC\mathbf{H}_3)_2$, 1.6–1.9 (m, 2H, $OCH_2C\mathbf{H}_2P$), 3–3.2 (m, 2H, $C\mathbf{H}_2NH$), 3.4 (d, 3H, $P(O)(OC\mathbf{H}_3)(OH)$), 3.8–4 (m, 4H, $OC\mathbf{H}_2$), 5.5 (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6 (s, H, $C\mathbf{H}_2{=}C(CH_3)$, 6.1 (m, 1H, N**H**), ^{31}**P** NMR (CD_3OD) δ (ppm): 28 (s).

Synthesis of the Diacid Product

In a two-necked, round-bottom flask (100 ml) equipped with a condenser and a septum, the phosphonated monomer was introduced in 25 ml of dry dichloromethane. After a 30 min argon purge, two molar equivalents of bromotrimethyl silane were added drop by drop. The mixture was stirred for 24 h at room temperature. Then, the silylated monomer was concentrated by evaporation of dichloromethane and dissolved in 25 ml of methanol. The solution was stirred for 2 h at room temperature. After evaporation of methanol the phosphonated monomer was obtained (90% yield).

IEMP C1. ^{1}**H** NMR (CD_3OD) δ (ppm): 1.5 (s, 3H, $CH_2{=}CC\mathbf{H}_3)_2$, 3.3 (q, 2H, $OCH_2C\mathbf{H}_2NH$), 4 (t, 2H, $OC\mathbf{H}_2CH_2NH$); 4.3 (d, 2H, $C\mathbf{H}_2P(O)(OH)_2$); 5.5 ppm (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6 (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6.1 (t, 1H, $CH_2N\mathbf{H}$). ^{31}**P** NMR (CD_3OD) δ (ppm): 20 (s).

IEMP C2. ^{1}**H** NMR (CD_3OD) δ (ppm): 1.5 (s, 3H, $CH_2{=}CC\mathbf{H}_3)_2$, 1.6–1.9 (m, 2H, $OCH_2C\mathbf{H}_2P$), 3–3.2 (m, 2H, $C\mathbf{H}_2NH$), 3.8–4 (m, 4H, $OC\mathbf{H}_2$), 5.5 ppm (s, H, $C\mathbf{H}_2{=}C(CH_3)$; 6 ppm (s, H, $C\mathbf{H}_2{=}C(CH_3)$, 6.1 (m, 1H, N**H**). ^{31}**P** NMR (CD_3OD) δ (ppm): 26 (s).

REFERENCES

[1] C. Brondino, B. Boutevin, J.-P. Parisi, and J. Schrynemackers, *J. Appl. Polym. Sci.*, **72,** 611 (1999).
[2] A. Riondel, R. Pirri, and T. Jeanmaire, *Eur. Pat. Appl.*, Ep 1201674, 9 pp. (2002).
[3] B. Youssef, L. Lecamp, W. El Khatib, C. Bunel, and B. Mortaigne, *Macromol. Chem. Phys.*, **204,** 1842 (2003).
[4] F. Ignatious, A. Sein, and J. Smid, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, **32,** 170 (1991).
[5] F. Ignatious, A. Sein, I. Cabasso, and J. Smid, *J. Polym. Sci., Part A: Polym. Chem.*, **31,** 239 (1993).
[6] S. Lin and I. Cabasso, *J. Polym. Sci., Part A: Polym. Chem.*, **35,** 889 (1997).
[7] E. P. Squiller and J. W. Rosthauser, *Polym. Mater. Sci. Eng.*, **55,** 640 (1986).
[8] E. P. Squiller and J. Rosthauser, *Modern Paint Coatings*, **77,** 28, 35 (1987).
[9] E. P. Squiller and J. W. Rosthauser, *Proceedings of the Water-Borne and Higher-Solids Coatings Symposium*, **14,** 460 (1987).
[10] N. Nakabayashi, K. Kimura, and S. Takahashi, *Jpn. Kokai Tokkyo Koho*, Jp 63107954, 7 pp. (1988).
[11] Y. H. Kim and H. S. Park, *Synlett.*, **3,** 261 (1998).
[12] A. G. Davies and R. J. Puddephatt, *J. Chem. Soc. [Section] C: Organic*, **12,** 1479–1483 (1968).
[13] R. B. Moffett, *J. Chem. Eng. Data*, **25,** 176 (1980).
[14] Q. S. Yu, B. Schonenberger, and A. Brossi, *Heterocycles*, **26,** 1271 (1987).
[15] A. Benalil, P. Roby, B. Carboni, and M. Vaultier, *Synthesis*, **9,** 787 (1991).
[16] R. W. Hoffmann, S. Dresely, and J. W. Lanz, *Chem. Ber.*, **121,** 1501 (1988).
[17] I. Muntean, J. M. Herdan, and G. Valeanu, *Rev. Roum. Chim.*, **33,** 467 (1988).
[18] F. Bachmann, D. Lohmann, and P. Chabrecek, *Eur. Pat. Appl.*, Ep 668294, 23 pp. (1995).
[19] R. D. Sayakhov, A. V. Mironov, V. I. Galkin, R. A. Cherkasov, G. A. Kutyrev, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **325,** 746 [Chem.] (1992).
[20] R. D. Sayakhov, A. V. Mironov, V. I. Galkin, G. A. Kutyrev, and R. A. Cherkasov, *Zhurnal Obshchei Khimii*, **63,** 2476 (1993).
[21] T. Jeanmaire, Y. Hervaud, and B. Boutevin, *Phosphorus, Sulfur, and Silicon*, **177,** 1137 (2002).
[22] T. Jeanmaire, Thèse, Université Montpellier II, Montpellier, France (2002).
[23] A. N. Pudovik, M. G. Zimin, and A. M. Kurguzova, *Zhurnal Obshchei Khimii*, **41,** 1964 (1971).
[24] D. K. Owens, *J. Appl. Polym. Sci.*, **19,** 3315 (1975).

[25] C. O. Kunz, P. C. Long, and A. N. Wright, *Polym. Eng. Sci.*, **12,** 209 (1972).
[26] K. Ishihara, Y. Iwasaki, S. Ebihara, Y. Shindo, and N. Nakabayashi, *Colloids Surf. B: Biointerfaces*, **18,** 325 (2000).
[27] Z. Liqun, G. S. Irwan, T. Kondo, and H. Kubota, *Eur. Polym. J.*, **36,** 1591 (2000).
[28] M. Gaboyard, Thèse, Universitè Montpellier II, Montpellier, France (2001).
[29] B. Boutevin, Y. Hervaud, T. Jeanmaire, A. Boulahna, and M. Elasri, *Phosphorus, Sulfur, and Silicon*, **174,** 1 (2001).
[30] C. Brondino, B. Boutevin, Y. Hervaud, N. Pelaprat, and A. Manseri, *J. Fluorine Chem.*, **76,** 193 (1996).
[31] B. Boutevin, B. Hamoui, and J. P. Parisi, *J. Appl. Polym. Sci.*, **52,** 449 (1994).
[32] R. Rabinowitz, *J. Org. Chem.*, **28,** 2975 (1963).