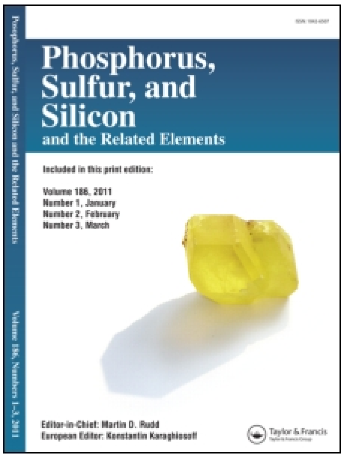

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SYNTHESIS OF α,ω-PHOSPHONATE POLYSTYRENE VIA DEAD END POLYMERIZATION

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To introduce phosphonate groups into polystyrene, two different routes were investigated, both using a conventional radical polymerization, the Dead End Polymerization (DEP). Route 1 described the synthesis of phosphonated azo-initiator by 4,4′-azobis cyanovaleric acid (ACVA) esterification; the new compound would then initiate the styrene DEP. Unfortunately, the esterification was not quantitative and the separation between ACVA and its phosphonated homologue remained unsuccessful. By route 2, we suggested the phosphonate group incorporation by esterification of α,ω-carboxy polystyrene previously obtained by DEP (initiated by ACVA). The esterification reaction was proved to be quantitative by NMR and FTIR techniques. The α,ω-phosphonate polystyrene synthesis was then realized from several α,ω-carboxy polystyrene with molecular weights ranging from 3000 up to 10000 g/mol.

Keywords: α,ω-Phosphonated polystyrene; chain end; Dead End Polymerization; esterification

INTRODUCTION

In an attempt to introduce phosphonate groups into polystyrene, which may be hydrolyzed into mono- or diacid form by hydrolysis of the phosphonic ester groups, two different pathways have been explored. The phosphonate group can be either incorporated during the styrene polymerization (or copolymerization) or via a polystyrene chemical modification. Firstly, radical polymerization was explored. Phosphonated styrene obtained by phosphonylation (reaction of chloromethylstyrene with alkylphosphites) was polymerized,[1] and the resulting polymer showed a very high thermal stability.[2] Then the telomerization of

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styrene[3] was carried out with phosphonated telogen agents such as $HP(O)(OEt)_2$. This technique led to phosphonate telomers with DPn of 34, resulting from the phosphonate telogen low-transfer constant at 130°C. The controlled radical polymerization via Madix route was also investigated by Rhodia Chemicals, using a phosphonate ester group containing a xanthate chain transfer agent.[4] Finally, following the same idea the anionic polymerization of styrene led to a phosphonated polystyrene by deactivation with dialkyl chlorophosphonates.[5] In an alternative route Wu et al.[6] copolymerized styrene with the diethylvinyl phosphonate. Our group[7] also synthesized dimethylvinylbenzyl phosphonate and copolymerized it with styrene, leading to a statistical block copolymer with number average molecular weight of 20000 g/mol.

The second way was the incorporation of phosphonate groups into the polymer chains after styrene polymerization.[8,9] Liu et al.[10] treated a poly(4-hydroxystyrene) (PS-OH) with dichlorophosphate, leading to a poly(phosphonated-styrene). The obtained polymer was considered to be an analogue of polystyrene and led to enhanced flame retardancy.[11–13]

In this article we suggested the phosphonate group incorporation via both pathways: by Dead End Polymerization (DEP) and by chemical modification of α,ω-carboxy polystyrene.

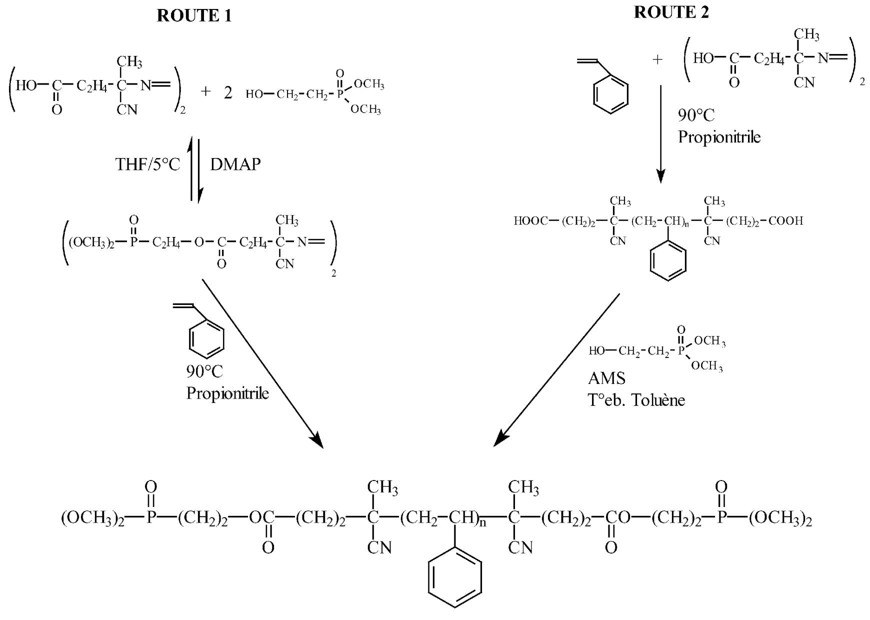
DISCUSSION

Two different ways were investigated to incorporate the phosphonate group (Scheme 1). The first one was the esterification of 4,4′-azobis cyanovaleric acid (ACVA), azo-initiator bearing an acid group, with dimethyl,2-hydroxyethylphosphonate. The radical polymerization of styrene under DEP conditions was then initiated by this new phosphonate initiator. The second way was the DEP reaction of styrene with 4,4′-azobis cyanovaleric acid followed by the esterification reaction of the α,ω-carboxy polystyrene with dimethyl,2-hydroxyethylphosphonate.

Route 1

Route 1 describes the synthesis of a phosphonate azo-initiator by ACVA esterification. This new compound will initiate the styrene radical polymerization, giving α,ω-phosphonate polystyrene via DEP conditions.

ACVA esterification was realized at low temperature (5°C) in tetrahydrofuran (THF) and activated by dimethylaminopyridine (DMAP). H_2O issued from the esterification was trapped by the 1,3-dicyclohexylcarbodiimide (DCCI) that was transformed into bicyclohexyl urea (BCHU). BCHU precipitated during the reaction,



SCHEME 1 Synthesis of α,ω-phosphonate polystyrene.

proving the esterification occurrence. After extraction of BCHU and evaporation of THF, the product was analyzed by ^{31}P NMR. The spectrum showed two signals, one characteristic of the phosphonate alcohol at 33.5 ppm and the other one of the phosphonate ACVA at 30 ppm. The phosphonate alcohol was in excess (1.2 to 1) compared to ACVA. However, the integration ratio showed that the alcohol signal was not only due to the alcohol excess but also to 20% of unreacted alcohol. This result means that about 20% of ACVA was not esterified. We tried to separate ACVA from its phosphonate homologue, otherwise ACVA would initiate styrene polymerization, which would lead to acid and phosphonated chain-end polystyrene. Recrystallization in methanol was attempted, but phosphonated ACVA was also soluble in methanol. Finally, a separation by silica gel chromatography was investigated with several eluents but remained unsuccessful.

Route 2

Route 2 leading to α,ω-phosphonate polystyrene synthesis is described in two steps: the first step is the styrene radical polymerization in DEP conditions initiated by ACVA, and the second step is the esterification reaction of the α,ω-carboxy polystyrene.

TABLE I Influence of C_0 Molar Ratio on Molecular Weight and Monomer Conversion (Experimental and Theoretical) Degree in DEP of Styrene with ACVA at 90°C

Experiment no	C_0 (%)	Mn (g/mol)	Experimental monomer conversion degree (%)	Theoretical monomer conversion degree (%)
1	0.2	10200	20	14
2	0.5	9800	35	32
3	0.8	6600	52	43
4	5	1900	62	65
5	10	1500	80	78

After 20 years of research in our group, a great deal is known about the DEP[14,15] especially concerning the DEP of styrene.[16–18] The synthesis of α,ω-carboxy polystyrene via DEP was previously realized by our group and is now well understood. This synthesis and especially its kinetic study were already published.[16–18] Several α,ω-carboxy polystyrenes of different molecular weights were obtained, depending on the chosen C_0 molar ratio ([ACVA]/[Styrene]). They are summarized in Table I. It is to be noticed that the diacid functionality was demonstrated by using different techniques such as ^{1}H NMR, conductimetric titrations, and Maldi-Tof analysis, and it was also published.[17]

The difficulty of Route 2 was the chain-end acid group esterification by 2-dimethylhydroxyethylphosphonate.

Methane sulfonic acid, usually used for high-temperature esterification, allowed acceleration of the reaction that occurred at toluene reflux. After 24 h, toluene was evaporated and the final product was precipitated in methanol, which solubilized residual dimethylhydroxyethylphosphonate. The final product was then analyzed by ^{31}P NMR.

The signal for dimethylhydroxyethylphosphonate situated at 33.5 ppm totally disappeared, and a new signal at 30.8 ppm appeared. This signal did not characterize the phosphonate alcohol. This new signal was characteristic of the ester groups. Indeed, FTIR analysis showed that the acid groups ($\upsilon = 1710$ cm^{-1}) totally disappeared, and a new band ($\upsilon = 1740$ cm^{-1}) characterized the ester groups and proved that the esterification reaction was quantitative.

^{1}H NMR for α,ω-phosphonate polystyrene was also realized (Figure 1). The spectrum especially showed the Ha methyl of the phosphonate group. This signal only characterized the phosphonate chain-end of polystyrene as dimethylhydroxyethylphosphonate was totally solubilized in methanol. By using the integration of Ha and aromatic protons He, α,ω-phosphonate polystyrene molecular weights were calculated. The results were reported in Table II and compared to those obtained by size-exclusion chromatography (SEC) for several

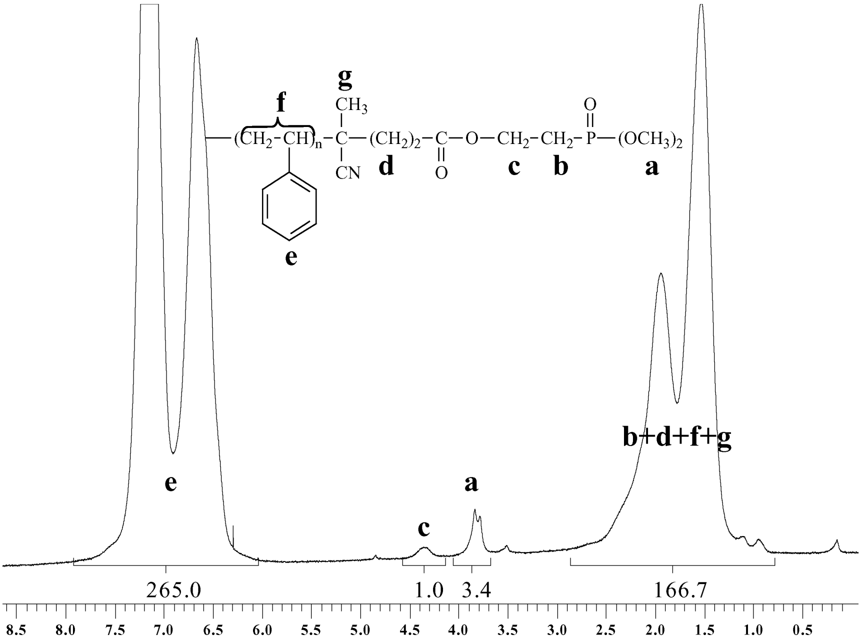


FIGURE 1 ^{1}H NMR spectrum ($CDCl_3$) of α,ω-phosphonate polystyrene.

polystyrene molecular weights. First, we can note that α,ω-carboxy polystyrene molecular weights were higher for C_0 5% and 10% than those reported in Table I. This was due to the methanol precipitation solubilizing the lower α,ω-carboxy polystyrene molecular weights. Indeed, the very low polydispersity indexes for these both experiments proved the oligomer extraction. Hence, Table II showed a slight increase in the molecular weight after esterification reaction. This increase was probably due to the phosphonate group chain-end. We also remarked

TABLE II Molecular Weights of Several α,ω-Phosphonate Polystyrene Calculated by SEC and ^{1}H NMR

	α,ω-Carboxy polystyrene			α,ω-Phosphonate polystyrene		
Experiment no	C_0 (%)	Mn (g/mol) from SEC	Ip from SEC	Mn (g/mol) from SEC	Mn (g/mol) from ^{1}H NMR	Ip from SEC
1	0.2	10200	1.56	10800	14000	1.70
2	0.5	9800	1.60	11900	11500	1.74
3	0.8	6600	1.40	6640	7050	1.41
4	5	4200	1.27	4550	5040	1.30
5	10	3300	1.25	3900	4000	1.37

that ^{1}H NMR and SEC gave similar Mn results, proving the phosphonated bifunctionality. Only ^{1}H NMR and SEC calculations for both No 1 and 2 experiments did not correlate very well. However, in both cases Mn were up to 10000 g/mol, which made the ^{1}H NMR molecular weight calculation difficult.

CONCLUSION

To introduce phosphonate groups into polystyrene two different routes were investigated, both using a conventional radical polymerization, the DEP. Route 1 described the synthesis of phosphonated azo-initiator by ACVA esterification; the new compound would then initiate the styrene DEP. Unfortunately, the ACVA esterification occurred at 80% yield. The separation between ACVA and its phosphonated homologue remained unsuccessful despite an attempted recrystalization and a chromatography separation. By route 2 we suggested the phosphonate group incorporation by esterification of α,ω-carboxy polystyrene. These diacid compounds were previously obtained by DEP (initiated by ACVA) with molecular weights ranging from 1500 up to 10000 g/mol. The esterification reaction was proved to be quantitative by NMR and FTIR techniques. Indeed, in FTIR the acid band totally disappeared. In ^{31}P NMR, a new signal characterized the phosphorus group after esterification. The α,ω-phosphonate polystyrene synthesis was then realized from several α,ω-carboxy polystyrene with molecular weights range from 3000 up to 10000 g/mol. The ^{1}H NMR allowed the molecular weight calculation and showed similar results with those from SEC.

EXPERIMENTAL

Styrene (99%), supplied by Aldrich, was distilled and stored under inert atmosphere at 5°C. ACVA (97%), DMAP, and DCCI were also supplied by Aldrich and used without further purification. Propionitrile, toluene, methanol, and THF were used as delivered by suppliers. Dimethyl-2-hydroxyethylphosphonate was previously synthesized in the laboratory.[19]

Synthesis of Phosphonated Azoinitiator

In a three-necked, round-bottom flask were introduced 3.0 g (10.71 mmol) of ACVA, 3.86 g (25.71 mmol) of dimethyl-2-hydroxyethylphosphonate, and 200 ml of THF. The mechanical stirring was fixed to 600 tr/min to homogenize the solution. The solution was then cooled to

5°C. A solution of 0.138 g (1.14 mmol) of DMAP and 5.304 g (25.71 mmol) of DCCI in 50 ml of THF was slowly added to the first solution. This addition was followed by the BCHU precipitation. The temperature reached 15°C. Precipitated BCHU was then filtrated and washed with 100 ml of THF (2 × 50 ml). The residue was evaporated and dried under vacuum (yield 80%).

^{31}P NMR (DMSO) δ(ppm): 30 (singlet, $(CH_3O)_2O$-**P**-C_2H_4-O-CO), 33.8 (singlet, $(CH_3O)_2O$-**P**-C_2H_4-OH).

Synthesis of Carboxy-Telechelic Polystyrene ($[M]_0 = 2$ mol/l, $C_0 = 10\%$)

In a 100 ml round-bottom flask were introduced 10 g of styrene (0.096 mol) and 2.7 g of ACVA (9.6×10^{-3} mol), and the solution was completed with 30 g of propionitrile. During ten minutes N_2 was bubbled into the solution. The polymerization was carried out at 90°C under inert atmosphere. The solution was cooled. Carboxy-telechelic polystyrene was precipitated in methanol and dried under vacuum (80% yield).

Synthesis of Phosphonated-Telechelic Polystyrene

In a 250 ml round-bottom flask equipped with a Dean-Stark were introduced 2.0 g (0.17 mmol) of carboxy-telechelic polystyrene (Mn = 11500 g/mol), 0.26 g (1;47 mmol) of dimethyl-2-hydroxyethylphosphonate, and 0.03 g (10% w/w with dimethyl-2-hydroxyethylphosphonate) of methanesulfonic acid and 150 ml of toluene. The esterification was carried out at toluene boiling temperature during 24 h. The solution was then cooled and the toluene evaporated. The phosphonate-telechelic polystyrene was precipitated with methanol. The final product was dried under vacuum (90% yield).

^{1}H NMR ($CDCl_3$) δ(ppm): 7 (multiplet, 5nH, aromatic protons), 4.3 (triplet, 4H, O-CH_2-CH_2), 3.7 (singlet, 12H, O-$\mathbf{CH_3}$), 1–2.5 (multiplet, 3nH, PS chain).

^{31}P NMR ($CDCl_3$) δ(ppm): 31 (singlet, **P**-$O(OCH_3)_2$).

Characterizations

Molecular weights ($\overline{Mn}$, number average molecular weight) were measured by SEC (Spectra-Physics SP 8430 RI Detector; SP 8800/8810 LC Pump) in THF with a polystyrene calibration.

The chemical structure of products was determined by ^{1}H and ^{31}P NMR (Bruker AC 200 MHz) at room temperature in $CDCl_3$ and dimethylsulfoxide (DMSO) solutions. The INVGATE procedure with delay D1 of 10s to get quantified the final yield.

Acid functionality of carboxy-telechelic polystyrene (CTPS) was determined by titration of CTPS in THF using a 0.05N methanolic potassium hydroxide solution. Titrations were made with phenolphtaleine by conductimetry with acetonitrile as solvent of CTPS.

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