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SYNTHESIS OF POLYMERS WITH PHOSPHONIUM END GROUPS BY ATOM TRANSFER RADICAL POLYMERIZATION

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Key Words: Atom Transfer Radical Polymerization (ATRP), End Group Modification, Phosphines, Phosphonium Salts

ABSTRACT

The end groups of polymers prepared by atom transfer radical polymerization (ATRP), are well-defined and determined by the initiator used, at least one of them is a halogen end group. The halogen end groups can be transformed to other functionalities such as phosphonium salts as demonstrated in this paper. Kinetic studies with the compounds 1-phenylethyl bromide and methyl 2-bromopropionate, models for the polystyrene and polyacrylate chain ends respectively, indicated that bromine end groups were readily transformed to phosphonium end groups upon the addition of phosphines. Stability tests with the obtained phosphonium salts showed that 1-phenylethyl trialkylphosphonium bromide was stable, even at higher temperatures and in the presence of free phosphines. The stability of the propionate analogue was limited due to the presence of the ester group in the molecule. Polystyrene and poly(methyl acrylate) phosphonium salts were

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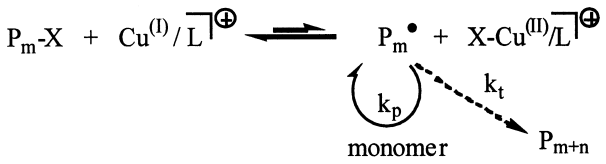
synthesized and the presence of the end groups was demonstrated by ^{1}H NMR and ESI-MS or MALDI-TOFMS.

INTRODUCTION

Atom transfer radical polymerization (ATRP) is a method to control radical polymerizations by establishing an equilibrium between growing and dormant chains using a metal/ligand complex (Scheme 1) [1-6]. The molecular weight of polymers such as polystyrenes or poly(meth)acrylates are predetermined by the ratio of the consumed monomer to the introduced initiator. The polydispersities are low ($M_w/M_n < 1.3$). The end groups of the polymers are defined by the initiator, usually an alkyl halide, because during the polymerization, the contribution of termination reactions is small, due to low radical concentrations. Therefore, the alkyl group of the alkyl halide initiator remains at one end of the produced polymer chain, while a halogen atom is present at the other end of the chain. For difunctional or multifunctional initiators, all chain ends contain halogen end groups with the initiator residue at the center of the polymer chain.

Polymers produced by ATRP can be considered as polymeric reagents because the active halogen end groups are available for subsequent reactions. Through modification of the end groups, by means of standard organic procedures, the desired functional groups such as azido, amino or allyl end groups can be introduced [7-9]. The derivatization reactions should be as free of side reactions as possible. Functionalized polymers have found widespread applications in organic synthesis and in related fields [10]. They have been used as stoichiometric reagents, as catalysts, as protecting groups, in ion exchange, in chromatography and in the field of agricultural chemicals. Functional polymers which have received considerable attention are those containing phosphorus-



Scheme 1. The synthesis of polymers by atom transfer radical polymerization (ATRP).

groups [11-12]. Polymer-bound alkylphosphines are useful in several reactions such as the Wittig reaction, conversion of alcohols to halides or the cleavage of ethers [13]. Polymer-bound alkyl phosphonium salts are ionomers and may also be used as phase transfer catalysts [14]. These polymeric catalysts have the advantage of being readily filtered from the reaction mixtures and phosphonium salts are preferred because they are generally chemically and thermally more stable than the corresponding ammonium salts.

The goal of this project was the synthesis of polymer-bound alkyl phosphonium salts by replacing the halogen end groups of polystyrenes and polyacrylates, prepared by ATRP, with phosphines. To demonstrate the feasibility of these displacement reactions, 1-phenylethyl bromide and methyl 2-bromo-propionate, models for polystyrene and polyacrylates respectively, were reacted with phosphines. Based on the results of the kinetic study of these model reactions, end group modification of the polymers with phosphines was performed. The transformation of the end groups was followed by ^{1}H NMR and ESI-MS or MALDI-TOFMS as it has been demonstrated that this mass spectrometry techniques serve as useful tools in the elucidation of polymer end groups [15-16].

EXPERIMENTAL

Materials

THF was distilled from Na/benzophenone. CuBr was purified by stirring in acetic acid, washing with methanol then drying. Styrene was passed through alumina, methyl acrylate was distilled. All other reagents, purchased from Aldrich or Acros, were used as received.

Analysis

GPC was carried out using PSS GPC columns (guard, 10^5Å, 10^3Å and 10^2Å) and was calibrated using linear polystyrene standards. A 300 MHz Bruker NMR spectrometer was used for ^{1}H NMR and ^{31}P NMR analysis. Phosphoric acid (85%) was used as external standard in the ^{31}P NMR analysis. MALDI-TOFMS spectra were obtained using a PerSeptive Biosystems Voyager Elite instrument, equipped with a N_2 laser at 337 nm (detection in linear mode). Trans-3-indole acrylic acid, 0.1 M in THF, was used as the matrix solution. ESI-MS was conducted using a Finnegan LCQ, equipped with an octapole and an ion trap mass analyzer. Polymer solutions, 10^{-4} M in methanol, were injected. The

spray voltage was 0.02 kV, the capillary voltage 0.07 V. Doping of the MALDI-TOFMS or ESI-MS samples was not required as the polymer-bound phosphonium salts were charged.

Synthesis of CH_3-CH(Ph)-P^+Bu_3 Br^- (1)

1-Phenylethyl bromide (5.4 mmol, 1 M solution) and tri-*n*-butylphosphine (6.48 mmol) were stirred in dry THF at room temperature for 48 hours. After evaporation of excess THF, the product was precipitated in *n*-hexanes.

^{1}H NMR ($CDCl_3$), δ: 7.30-7.50 (5H, Ph), 4.80 (1H, -CH-), 2.52-2.25 (6H, P^+-CH_2-), 1.75 (3H, CH_3-), 1.45 (12H, -CH_2-CH_2-), 0.93 (9H, -CH_3) ppm. ^{31}P NMR ($CDCl_3$), δ: 34.9 ppm.

Synthesis of CH_3-CH($COOCH_3$)-P^+Bu_3 Br^- (2)

The synthesis was similar to (**1**) but methyl 2-bromopropionate was used instead of 1-phenylethyl bromide.

^{1}H NMR ($CDCl_3$), δ: 4.70 (1H, -CH-), 3.8 (3H, -$COOCH_3$), 2.55 (6H, P^+-CH_2-), 1.38-1.68 (3H, CH_3- and 12H, -(CH_2-CH_2)-), 0.97 (9H, -CH_3) ppm. ^{31}P NMR ($CDCl_3$) δ: 36.5 ppm.

Synthesis of CH_3-CH($COOCH_3$)-P^+Ph_3 Br^- (3)

The synthesis was similar to (**1**) except that methyl 2-bromopropionate and triphenylphosphine were used as reagents.

^{1}H NMR ($CDCl_3$) δ: 7.50-8.05 (15H, Ph), 7.12 (1H, -CH-), 3.57 (3H, -$COOCH_3$), 1.72 (3H, CH_3-) ppm. ^{31}P NMR ($CDCl_3$) δ: 28.3 ppm.

Stability Tests

Each of the compounds (**1**, 2 or **3**, 50 mg in an NMR-tube) was kept in an oil bath at 80˚C and 120˚C. In the experiments where PPh_3 was added, dry THF was used as a solvent. After 8 hours, the ^{1}H NMR spectrum was compared to that of the original product.

Kinetic Measurements

Approximately 50 mg of alkyl halide (methyl 2-bromopropionate or 1-phenylethyl bromide) was dissolved in acetonitrile (0.3 M solution) and 1 equiv-

alent of phosphine was added. The solutions were kept at room temperature or in an oil bath at 80˚C and, at regular time intervals, the conversion was measured using ^{1}H NMR.

Synthesis of Polymers by ATRP

Degassed methyl acrylate or styrene (5 ml) was mixed with ethylene carbonate or p-dimethoxybenzene (5 g) respectively and CuBr, 2,2'-bipyridine (bpy) and initiator (methyl 2-bromopropionate (MA) or 1-phenylethyl bromide (Sty)) in a ratio 0.5/1.5/1 were added. After the polymerization, at 90˚C for acrylate and 110˚C for styrene, the reaction mixtures were diluted with THF and passed through alumina. Poly(methyl acrylate) (M_n = 2270, M_w/M_n = 1.12) was precipitated in *n*-hexanes, polystyrene (M_n = 1650, M_w/M_n = 1.09) in methanol.

The Transformation of the Polymer End Groups

Poly(methyl acrylate) with bromine end groups, was dissolved in dry THF and a 10-fold excess of tri-*n*-butylphosphine was added. After stirring for 48 hours at 30˚C, the polymer was purified by precipitation in *n*-hexanes.

$$\text{MALDI-TOFMS (pMA- } P^+Bu_3\text{): } m/z = [87 + n \times 86 + 202]^+$$

^{1}H NMR (pMA-P^+Bu_3): The complete substitution of the bromine by phosphonium end groups was observed by comparing the ratio of integrations for respectively CH_3 (initiator) at 1.15 ppm and 3 x CH_3 (Bu-groups) at 0.95 ppm.

Polystyrene with bromine end groups was reacted with tri-*n*-butylphosphine under similar reaction conditions.

$$\text{ESI-MS (pSty- } P^+Bu_3\text{): } m/z = [105 + n \times 104 + 202]^+$$

RESULTS AND DISCUSSION

In order to investigate the reactivity of their end groups towards phosphines, model reactions with 1-phenylethyl bromide and methyl 2-bromopropionate, model compounds for polystyrene and poly(methyl acrylate) respectively, were performed. The models were reacted with tri-*n*-butylphos-phine or triphenylphosphine.

TABLE 1. pK_a Values of Phosphines and Amines

Amines	pK_a	Phosphines	pK_a
$MeNH_2$	10.62	$MePH_2$	-3.2
Me_2NH	10.64	Me_2PH	3.9
Me_3N	9.76	Me_3P	8.65
		Bu_3P	8.43
		Ph_3P	2.73

Trisubstituted phosphines R_3P (R=alkyl, aryl) carry a lone pair of electrons which provides basicity and nucleophilicity [17-18]. The basicity of the phosphines, in contrast to the amines, depends largely on their degree and nature of substitution. As an illustration, some pK_a values of phosphines and amines are shown in Table 1 [19-20]. Triphenylphosphine is a weaker base than tri-*n*-butylphosphine. The lower basicity is the result of steric effects, i.e. phenyl groups are bigger than alkyl groups, and the conjugation between the lone-pair on phosphorus and the phenyl ring [20].

Phosphines are generally weaker bases than amines, however, they are better nucleophiles. In contrast to the corresponding amines, the rate of the reaction of phosphines with alkyl halides increases considerably, together with increasing pK_a. Tri-*n*-butylphosphine is a stronger nucleophile than triphenylphosphine.

In anhydrous solvents, tertiary phosphines undergo a Menshutkin-type reaction with alkyl halides, resulting in quaternary phosphonium salts. The reaction displays S_N2 characteristics. Under aqueous conditions, the formation of phosphine oxide may be observed [19].

$$Ph_3P + RCH_2Br \rightarrow Ph_3P^+CH_2R\ Br^-$$

1-Phenylethyl bromide and methyl 2-bromopropionate were reacted with tri-*n*-butylphosphine and triphenylphosphine and the reaction products were isolated by precipitation in *n*-hexanes. The obtained phosphonium salts were characterized by ^1H- and ^{31}P NMR (see Experimental). After the reaction of methyl 2-bromopropionate with tri-*n*-butylphosphine, the chemical shift of -CH(COOMe)-P^+Bu_3 was observed at 4.70 ppm. After the reaction with triphenylphosphine, the chemical shift of -CH(COOMe)-P^+Ph_3 was observed at 7.12 ppm. The chemical shift of -CH(Ph)-P^+Bu_3 was observed at 4.80 ppm.

To investigate the stability of the phosphonium salts, the products were heated in an oil bath at 80˚C or 120˚C, in the absence and in the presence of free phosphine. After 8 hours, the products were analyzed by ^{1}H NMR. The results of the stability tests are summerized in Table 2.

According to the ^{1}H NMR data, the products **1**, **2** and **3** (Table 2) were stable at 80˚C. At 120˚C however, decomposition of **2** and **3** was observed. In both cases, the ^{1}H NMR spectra indicated the loss (>90%) of the methyl ester as the methyl ester peak around 3.6 ppm had disappeared.

In the presence of an excess of phosphine, **2** and **3** were not stable at 80˚C. In the ^{1}H NMR spectra, methyl ester peaks were absent. Although the nature of the decomposition products was not investigated, it is known that tervalent organophosphorus compounds can attack a carbonyl carbon or oxygen. After reaction with the carbonyl carbon, the initial P-C-O adducts may rearrange to P-O-C compounds. An important factor in this process is the formation of a very strong P-O bond, which has a bond dissociation energy of approximately 200 kJ mol^{-1}[20].

At room temperature, a methyl ester is not attacked by phosphines. When methyl propionate and tri-*n*-butylphosphine were dissolved in dry THF and stirred at room temperature for 24 hours, no reaction occurred. This suggested that at ambient temperature, an excess of phosphines could be used to accelerate the reaction between methyl 2-bromopropionate and phosphines.

To investigate the rate of the reaction between the model compounds and the phosphines, kinetic measurements were performed. 1-Phenylethyl bromide or methyl 2-bromopropionate (0.3 M solution in acetonitrile) were reacted with triphenylphosphine or tri-*n*-butylphosphine, at 25˚C and at 80˚C. For the solvent, acetonitrile was chosen because polar solvents facilitate the reaction

TABLE 2. The Stability of the Phosphonium Salts was Studied by Keeping Them at Different Temperatures, in Absence or Presence of Excess Phosphine. After 8 Hours, the Products were Analyzed by ^{1}H NMR

#	Product	80°C	120°C	80°C + 1eq. PR_3	120°C + 1 eq. PR_3
1	$CH_3CH(Ph)P^+Bu_3$	s	s	s	s
2	$CH_3CH(COOMe)P^+Bu_3$	s	u	u	u
3	$CH_3CH(COOMe)P^+Ph_3$	s	u	u	u

s = stable, less than 5% decomposition in 8 hours

u = unstable, more than 90% decomposition in 8 hours

between alkyl halides and phosphines. A good alternative for acetonitrile is tetrahydrofuran. DMSO however seems to interact with the phosphines, especially at higher temperatures. All reactions were followed by ^{1}H NMR.

The reaction of 1-phenylethyl bromide with triphenylphosphine was very slow at 25˚C (Figure 1); only 20% conversion was obtained after 24 hours. At 80˚C, the reaction was much faster; 92% conversion after 24 hours. During the reaction however, a minor amount of styrene (5%) was formed, due to elimination.

The reaction of 1-phenylethyl bromide with tri-*n*-butylphosphine at room temperature was significantly faster than the reaction with triphenylphosphine. Fifty percent conversion was reached after 4 hours, after which the reaction slowed down. As mentioned before, tri-*n*-butylphosphine is a stronger nucleophile than triphenylphosphine, which explains the slow rate with triphenylphosphine. At 80˚C, 96% conversion was obtained after 24 hours. However, 30% of the resulting product was styrene, formed by elimination. The higher percentage of elimination can be explained by the higher basicity of tri-*n*-butylphosphine.

The reaction of triphenylphosphine with methyl 2-bromopropionate at 25˚C was relatively slow but faster than the reaction with 1-phenylethyl bromide (Figure 2). After 24 hours, 30% conversion was obtained. At 80˚C, the reaction

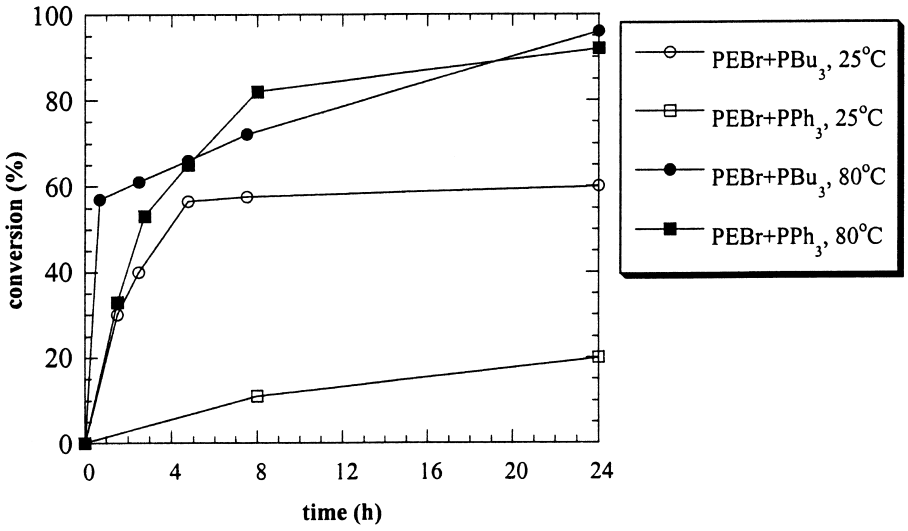


Figure 1. The kinetics of the reactions of 1-phenylethyl bromide (0.3 M in acetonitrile) with phosphines (1 eq.), followed by ^{1}H NMR.

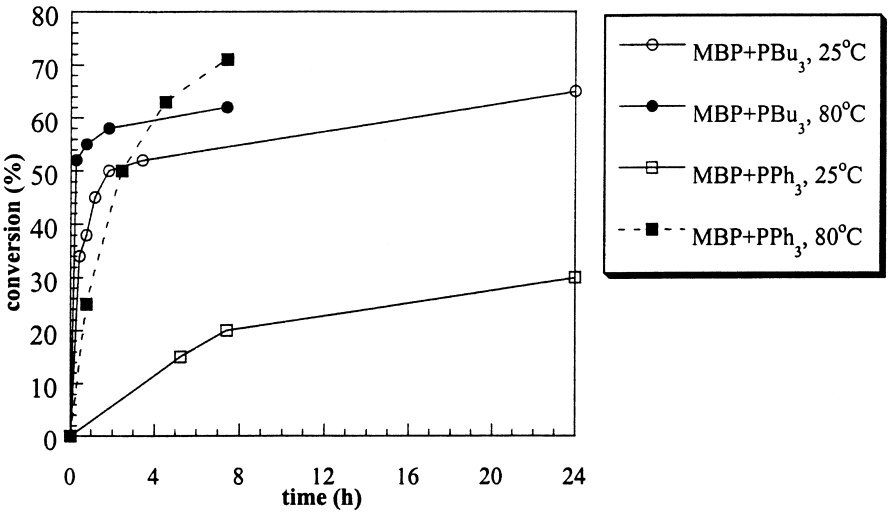


Figure 2. The kinetics of the reactions of methyl 2-bromopropionate (0.3 M in acetonitrile) with phosphines (1 eq.), followed by ^{1}H NMR.

proceeded faster but after 4 hours, the ^{1}H NMR spectrum indicated that the product started to decompose as signified by the methyl ester peak diminishing. After 7.5 hours, 27% unreacted substrate was left and 61% phosphonium salt was obtained. After 24 hours at 80˚C, the product was almost completely decomposed, the methyl ester peak had almost completely disappeared in the ^{1}H NMR spectrum.

The reaction of methyl 2-bromopropionate with tri-*n*-butylphosphine at 25˚C proceeded, as expected, faster than the reaction with triphenylphosphine (65% conversion after 24 hours). At 80˚C, the reaction proceeded faster but after 4 hours, again, decomposition of product was observed.

The rate constants for all model reactions were calculated, using the initial slopes of the second-order plots. The results are summarized in Table 3.

The results of the model studies can be extrapolated to the bromine end groups of polystyrene or poly(methyl acrylate). Thus, the reactions with triphenylphosphine are expected to occur slowly, especially at room temperature. At higher temperatures however, the reaction of triphenylphosphine with poly(methyl acrylate)-Br may result in side reactions, i.e. decomposition of the phosphonium end groups. The reactions with tri-*n*-butylphosphine should occur faster and could be performed at room temperature. At higher temperatures, elimination at the polystyrene chain ends and decomposition of the poly(methyl acrylate)-phosphonium salt could occur.

TABLE 3. The Rate Constants for the Reactions of 1-Phenylethyl Bromide (1-PEBr) and Methyl 2-Bromopropionate (MBP) with Phosphines in Acetonitrile

	1-PEBr, k (10^{-4} M^{-1} s)	MBP, k (10^{-4} M^{-1} s)
PBu_3, 25°C	2.5	4.7 2.8[x]
PBu_3, 80°C	17	≥ 40*
PPh_3, 25°C	0.1	0.3
PPh_3, 80°C	3.7	≥ 3.5*

*decomposition of product observed

[x]reaction performed in dry THF

Poly(methyl acrylate) (M_w= 2500, M_w/M_n= 1.1) with a bromine chain end was reacted with a 10-fold excess of tri-*n*-butylphosphine at 30˚C for 48 hours. After purification, the presence of the phosphonium end groups was observed with MALDI-TOFMS (Figure 3) and ^{1}H NMR (see Experimental). The sample for MALDI-TOFMS was prepared using trans-3-indole acrylic acid as matrix, and doping was not necessary as the polymer itself is positively charged. The peaks in the spectrum correspond within an error range of ± 3 a.m.u. to poly(methyl acrylate)-bound tri-*n*-butylphosphonium, m/z = [87 (CH_3-CH(COOMe)-) + n x 86 (-CH_2-CH(COOMe)-) + 202 (-PBu_3)]$^+$. The quantitative analysis of the end groups was performed with ^{1}H NMR. The complete substitution of the bromine by phosphonium end groups was observed by comparing the ratio of integrations for respectively the CH_3- peak (initiator) at 1.15 ppm and the peak at 0.95 ppm (3x CH_3 of the butyl-groups).

Styrene was polymerized in p-dimethoxybenzene using CuBr/bpy as catalyst system and the obtained polystyrene (M_n= 1650, M_w/M_n= 1.09), with bromine end groups was purified by precipitation in methanol. The polystyrene was further reacted with a 10-fold excess of tri-*n*-butylphosphine at 30˚C in dry tetrahydrofuran. After stirring for 48 hours, the phosphonium end functionalized polymer was characterized using ESI-MS (Figure 4). The peaks in the spectrum corresponded to polystyrene-bound tri-*n*-butylphosphonium, m/z = [105 (CH_3-CH(Ph)-) + n x 104 (-CH_2-CH(Ph)-) + 202 (-PBu_3)]$^+$.

CONCLUSION

The bromine end groups of polymers prepared by ATRP were substituted by phosphines to form polymer-bound alkyl phosphonium salts. Model stud-

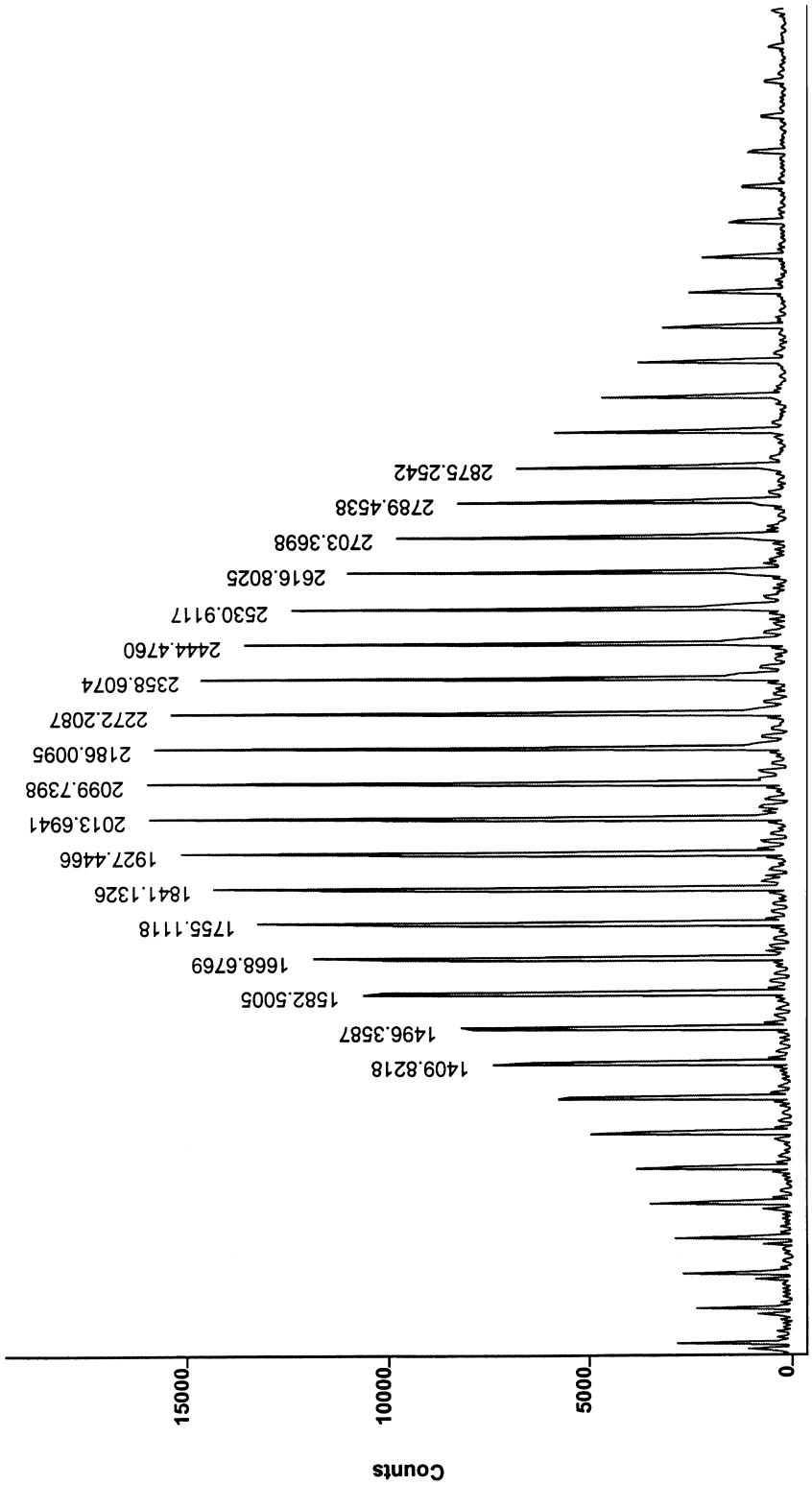


Figure 3. MALDI-TOFMS spectrum of pMA-P^+Bu_3.

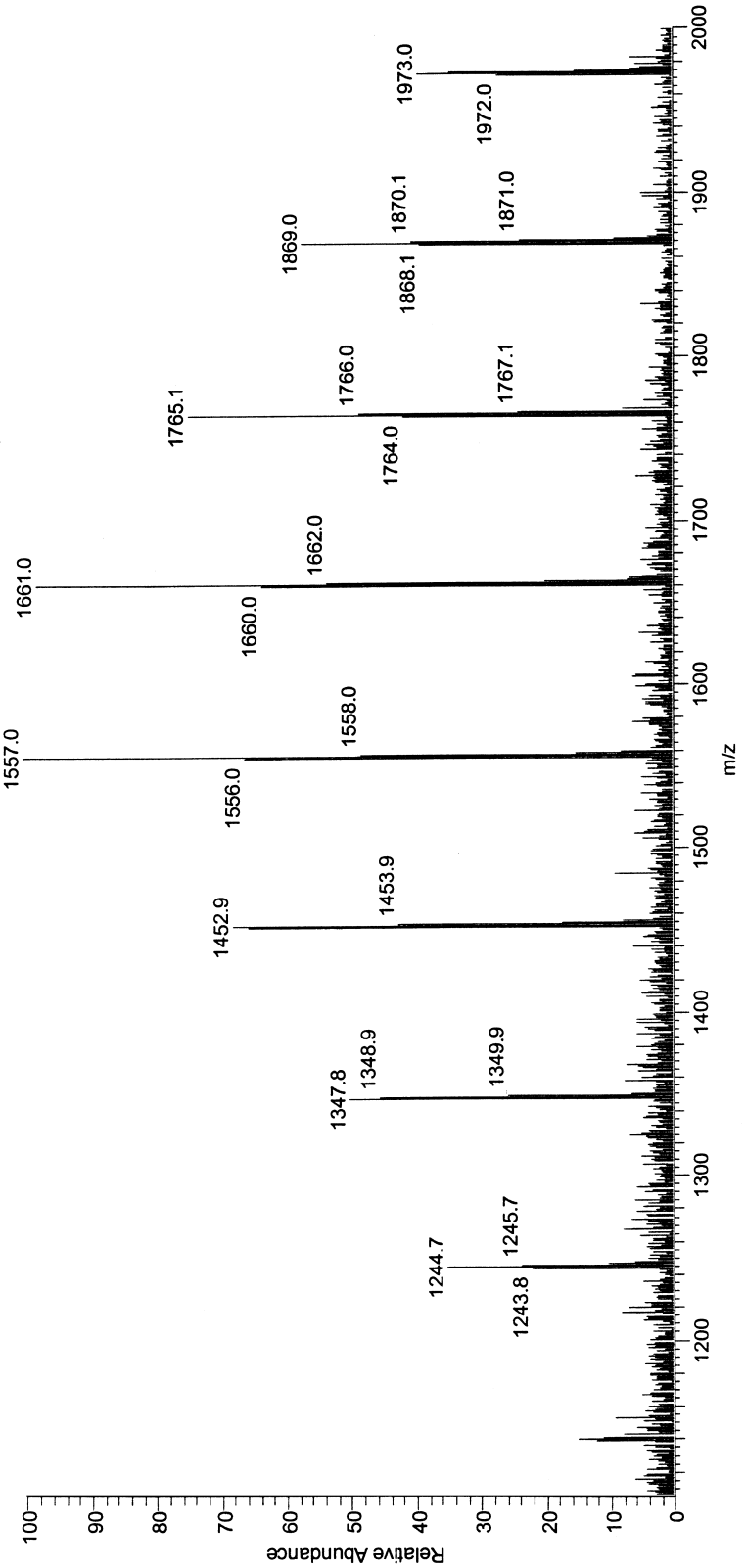


Figure 4. ESI-MS spectrum of polystyrene-$P^{+}Bu_3$.

ies indicated that tri-*n*-butylphosphine was a good nucleophile for the displacement of the bromine end groups. Stability tests with the model compounds indicated that polystyrene-bound alkyl phosphonium salts were stable, even at elevated temperatures and in the presence of free phosphines. Polyacrylate-bound alkyl phosphonium salts have a limited stability due to the presence of the ester groups. Poly(methyl acrylate) and polystyrene with bromine end groups were reacted with tri-*n*-butylphosphine and the substituted polymers were analyzed by ^{1}H NMR and mass spectrometry techniques.

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