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Synthesis of azido end-functionalized polyacrylates via atom transfer radical polymerization

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Summary

Atom transfer radical polymerization (ATRP) was demonstrated to yield well-defined polyacrylates with halogen end groups. These halogen end groups were transformed to azide groups which were subsequently reduced into amino groups. The replacement of the halogen end groups by azide groups was obtained either by using sodium azide or by treatment with trimethylsilyl azide in the presence of both stoichiometric and catalytic amounts of tetrabutylammonium fluoride (TBAF). The azide end groups were reacted with triphenylphosphine in order to obtain iminophosphorane groups which were then hydrolyzed yielding amino terminated polyacrylates.

Introduction

The controlled polymerization of acrylates has been a major challenge in synthetic polymer chemistry. Acrylates cannot polymerize by cationic polymerization, in anionic
polymerization several side reactions occur and although acrylates polymerize well by radical polymerization, control of the radical polymerization has been difficult. Recently however, several methods to control radical polymerizations have been reported (1-7). Among them, atom transfer radical polymerization (ATRP) has been shown to be one of the most effective methods for the controlled polymerization of acrylates and methacrylates (4-15). The key mechanism of ATRP, shown in Figure 1, is
the reversible formation of radicals from alkyl halides accompanied by reduction/oxidation of the copper halide catalyst which is complexed with 2,2'-bipyridine (bpy) derivatives (5,6). ATRP has provided well-defined polymers with narrow molecular weight distribution ($1.04 < M_w / M_n < 1.5$) and molecular weights predetermined by the ratio of concentrations of reacted monomer and introduced initiator ($DP = \Delta[M]/[I]_O$) (6,7).

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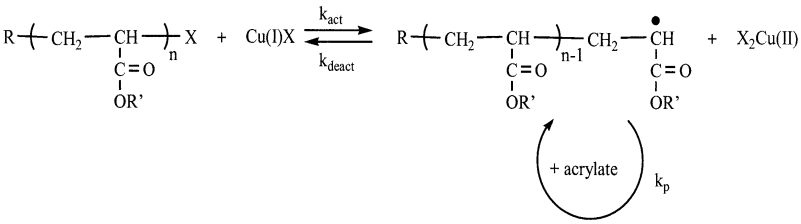

Figure 1 : Mechanism of ATRP

With ATRP, the alkyl group of the alkyl halide initiator remains at one end of the produced polymer chain, a halogen atom is quantitatively transferred to the other end of the chain (6). By replacement of the halogen end group, several functional groups can be introduced at the polymer chain end. An interesting functional group transformation is the one to azide end groups. Azide groups can produce nitrenes on thermolysis or photolysis, or can be converted to other functionalities such as amines, nitriles, isocyanates, etc.

Until now, only azide *side*-functionalized polyacrylates have been prepared by copolymerization of azide containing acrylates with other acrylates and have been used as photoresists (16,17). Azide *end*-functional polyacrylates have not been prepared before.
Recently, we reported the transformation of halogen end groups to azides on polystyrene using trimethylsilyl azide in the presence of tetrabutylammonium fluoride (18). In this paper, we report the azidation of bromo-end polyacrylates to yield azide end-functionalized polyacrylates. The azide end groups were subsequently reacted with triphenylphosphine with the formation of iminophosphorane terminated acrylates. The iminophosphorane end groups were then hydrolyzed yielding amino terminated acrylates.

Experimental

Materials

n-Butyl acrylate, methyl acrylate and methyl 2-bromopropionate were purified by distillation. Benzene was distilled from CaH_2, THF from Na/benzophenone. CuBr was purified by stirring in acetic acid, washing with methanol then drying. 4,4'-Di(5-nonyl)-2,2'-bipyridine (dNbpy) was prepared by coupling of 4-(5-nonyl)pyridine with Pd/C catalyst. All other reagents were used as received.

Analysis

GPC measurements were carried out using a Waters 510 liquid chromatography pump equipped with four Phenogel columns (100Å, 1000Å, linear and guard) in series with a Waters 410 differential refractometer and a Waters 991 UV detector. Calibration was based on linear polystyrene standards. A 300 MHz Brüker NMR spectrometer was used for ^{1}H-NMR analysis. GC measurements were carried out using a Shimadzu GC-14A equipped with a wide-bore capillary column (J&W Scientific, DB-WAX). An ATI

Mattson Infinity FT-IR spectrometer was used for IR analyses. Mass spectra were obtained using Matrix Assisted Laser Desorption Ionization, Time of Flight Mass Spectrometry (MALDI-TOFMS).

Preparation of bromo end-functionalized poly(butyl acrylate)
A dry flask, charged with CuBr (0.250 g; 1.74×10^{-3} mol) and di(5-nonyl)-2,2'-bipyridine (dNbpy) (1.42 g; 3.48×10^{-3} mol) was sealed with a rubber septum and cycled three times between vacuum and argon to remove oxygen. Degassed benzene (10.0 ml), n-butyl acrylate (10.0 ml; 6.98×10^{-2} mol), *n*-dodecane (0.4 ml; GC standard) and methyl 2-bromopropionate (0.194 ml; 1.74×10^{-3} mol) were added and the flask was immersed in an oil bath held at 80 °C by a thermostat. Conversion of the polymerization was determined by GLC measurement of the sampled reaction mixture. After heating was stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was passed through a short alumina column and the solvent evaporated. The resulting polymer contained a small amount of dNbipy and *n*-decane but was used without further purification. The polymer had M_n = 4,700 and M_w/M_n = 1.09 for theoretical M_n = 4,600.

Preparation of bromo end-functionalized poly(methyl acrylate)
The procedure described above was used for the preparation of poly(methyl acrylate). The product was purified by reprecipitation into n-hexane. The polymer had M_n = 3,400 and M_w / M_n = 1.2 for theoretical M_n = 3,600. A second batch of poly(methyl acrylate) had M_n = 1850 and M_w / M_n = 1.1.

Azidation of methyl 2-bromopropionate
Method 1: To a solution of methyl 2-bromopropionate (1.0 ml, 9.0 mmol) in dimethylformamide (DMF) (3 ml), sodium azide (0.64 g, 9.9 mmol) was added. After stirring the reaction mixture for 5h at room temperature, ether and water were added and the organic layer was extracted for another three times with water and dried over $MgSO_4$.
Method 2: A dry round-bottom flask was charged with methyl 2-bromopropionate (0.56 ml; 5.0 mmol) and trimethylsilyl azide (1.0 ml; 7.5 mmol) under argon. Upon addition of a solution of tetrabutylammonium fluoride (TBAF) (1.0 M THF solution; 7.5 ml; 7.5 mmol), an exothermic reaction occurred. After stirring for one day, the reaction mixture was diluted with Et_2O, and then passed through a short silica gel column and evaporated.
Method 3: A dry round-bottom flask was charged with methyl 2-bromopropionate (0.56 ml; 5.0 mmol), trimethylsilyl azide (0.73 ml; 5.5 mmol) and potassium fluoride (0.32 g; 5.5 mmol) under argon. To the mixture was added a solution of TBAF (1.0 M THF solution; 0.5 ml; 0.5 mmol). The workup was done as described above.
^{1}H-NMR ($CDCl_3$) δ: 3.94 (q, 1H, J = 7 Hz), 3.78 (s, 3H), 1.46 (d, 3H, J = 7 Hz).
FT-IR (cm^{-1}): 2110 (s), 1740 (s).

Azidation of bromo end-functionalized poly(n-butyl acrylate) or poly(methyl acrylate)
The procedures used for the azidation of the polyacrylates were the same as these used for the azidation of methyl 2-bromopropionate. The poly(n-butyl acrylate) derivative was purified by diluting the reaction mixture with *n*-hexane, then passed through a short silica gel column. After evaporation of the solvent, the presence of the azide end groups were observed by FT-IR (cm^{-1}): 2112 (s), 1735 (s). The poly(methyl acrylate) was purified by reprecipitation in n-hexanes and filtration through a short alumina column.

Calibration for FT-IR
Methyl 2-azidopropionate and bromo end-functionalized poly(n-butyl acrylate) were mixed in several ratios. The mixtures were prepared in $CHCl_3$ and FT-IR spectra were made. The integrations of the peaks corresponding to the azide and carbonyl groups were compared.

Reaction of azido end-functionalized poly(methyl acrylate) with triphenylphosphine
To a solution of poly(methyl acrylate)-N_3 in dry THF, triphenylphosphine (1.2 equivalents for each end group) was added. After stirring the reaction mixture at room temperature overnight, the product was purified by reprecipitation in n-hexane. Complete conversion of the azido end groups into iminophosphorane groups was observed in ^{1}H-NMR by comparing the integration of the following peaks : δ=7.3 to 7.7 ppm (3 phenyl groups) and δ=1.15 ppm (CH_3 of the initiating group).

Hydrolysis of the iminophosphorane end groups of poly(methyl acrylate)
To a solution of poly(methyl acrylate)-N=PPh_3 in THF, a 10-fold excess of water was added. The reaction mixture was stirred for 48h at room temperature and the product was purified by reprecipitation in n-hexanes. Analysis of the product was done by MALDI-TOFMS.

MALDI-TOFMS analysis
Samples were prepared mixing the matrix solution (a 0.1 M solution of trans-3-indole acrylic acid in THF, doped with a 0.1 M solution of sodium trifluoroacetate in THF) and the polymer solution (4 mg polymer per 1 ml THF).

Results and discussion
The preparation of bromo end-functionalized poly(n-butyl acrylate) and poly(methyl acrylate) was performed by ATRP using methyl 2-bromopropionate as initiator (Figure 2). During the polymerization reactions, a nearly linear increase in the first order kinetic plots was observed; n-butyl acrylate is shown as a representative example (Figure 3). The controlled polymerization afforded polyacrylates which had pre-defined M_n values (DP= $\Delta[M]/[I]_O$) and very low polydispersities, M_w / M_n <1.1 (Figure 4). ^{1}H-NMR spectroscopy showed no evidence of elimination of the bromide end group. These results indicated that the polymers had the structure as drawn in Figure 2.

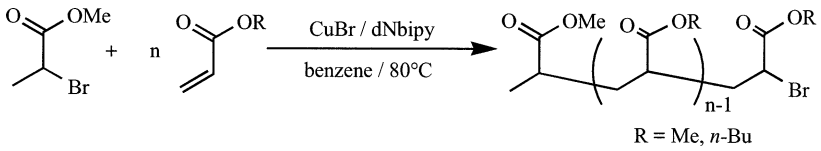

Figure 2 : ATRP of the polyacrylates

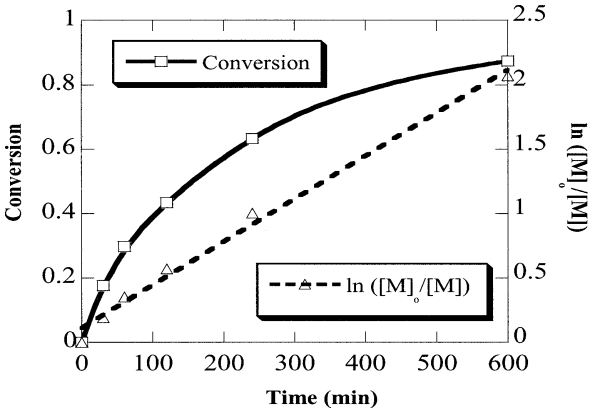

Figure 3 : Kinetics for the ATRP of n-butyl acrylate in benzene at 80°C.

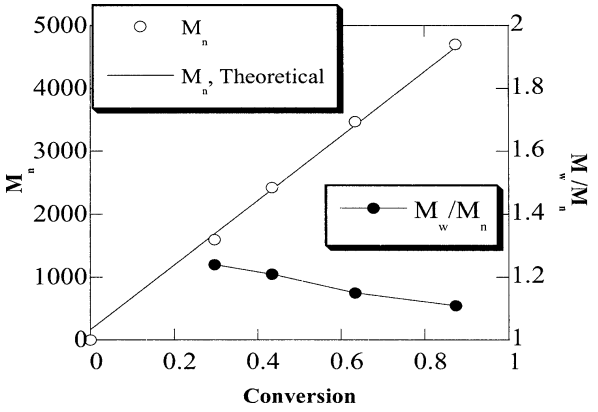

Figure 4 : M_n and M_w/M_n versus conversion for ATRP of n-butyl acrylate.

As a model for the azidation of bromo end-functionalized polyacrylates, the azidation of methyl 2-bromopropionate was studied. The most general synthesis of aliphatic azides constitutes the direct introduction of the azido group by nucleophilic displacement with the azide ion (19). Therefore, methyl 2-bromopropionate was stirred at room temperature in DMF with 1.1 equivalent of sodium azide (Figure 5). These mild conditions were suitable because substitution by azide ion occurs more readily when the alkyl substrate bears an electron-withdrawing group (20). ^{1}H-NMR confirmed that after 5 hours stirring, the conversion was quantitative : the peak corresponding to the CH-proton shifted completely from 4.40 ppm in methyl 2-bromopropionate to 3.94 ppm in methyl 2-azidopropionate.
In an alternative procedure which avoided the use of DMF as solvent and led to homogeneous reaction mixtures, the organic azide, trimethylsilylazide was used as azide source. Methyl 2-bromopropionate was successfully converted to methyl 2-azidopropionate in a mixture of 1.5 equivalents of trimethylsilyl azide and TBAF (Figure 5). When a catalytic amount of TBAF (0.1 equivalent) was used, potassium fluoride was required in stoichiometric amounts. Complete conversion without occurrence of elimination was observed in ^{1}H-NMR.
Both azidation procedures were succesfully applied to the polyacrylates.

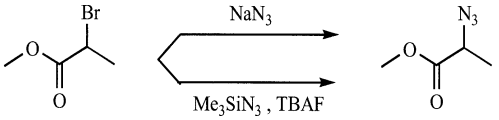

Figure 5 : The synthesis of methyl 2-azidopropionate

Unlike polystyrene, quantitation of the azidation by ^{1}H-NMR was difficult for polyacrylates, as the peak from alkoxy groups of the acrylates coincided with the peak of the methine proton geminal to the azide. Using methyl 2-azidopropionate and bromo end-functionalized poly(n-butyl acrylate), a calibration curve for FT-IR was made to quantify the azide group content in poly(*n*-butyl acrylate). Mixtures of the compounds were measured by FT-IR, and integrations of the two peaks assigned to the azide and carbonyl groups were compared with one another. The calibration curve for the molar ratio N_3/COO versus ratio of integration N_3/COO has a slope of 7.286 and an intercept of 0.016341.

After azidation of the bromo end groups of poly(*n*-butyl acrylate) with trimethylsilylazide/TBAF, the product was analyzed by FT-IR. The ratio of the integration of the azido (2112 cm^{-1}) and carbonyl peaks (1735 cm^{-1}) was 0.059. Based on the calibration curve, it was calculated that the ratio of the azido group to butyl acrylate units was 0.026, which was in agreement with the expected value of N_3 / *n*-butyl acrylate = 0.028.
After azidation of the bromo end groups of poly(methyl acrylate), the ratio of the integrations of the peaks corresponding to the azido (2113 cm^{-1}) and carbonyl groups (1736 cm^{-1}) was 0.055. Based on the calibration curve, it was calculated that the ratio

of the azido group to methyl acrylate units was 0.024, which corresponded perfectly to the predicted value of N_3/ methyl acrylate = 0.024.

Azido terminated poly(methyl acrylate) (M_n = 1850, M_w / M_n = 1.1) was further used to prepare amino end-functionalized polyacrylate. One of the mildest and most selective routes to convert azides to amines involves the reaction of the azides with triphenylphosphine to form the corresponding iminophosphorane groups which are hydrolyzed subsequently (Figure 6) (21).

$$RN_3 + Ph_3P \longrightarrow RN{=}PPh_3 \xrightarrow{H_2O} RNH_2$$

Figure 6 : Reduction of the azide end groups to amines via the Staudinger process and subsequent hydrolysis of the obtained iminophosphorane end groups

Hence, azide end-functionalized poly(methyl acrylate) was reacted with a slight excess of triphenylphosphine in dry THF. Complete conversion of the azide end groups into iminophosphorane end groups was observed in ^{1}H-NMR. The iminophosphorane end groups were finally hydrolyzed by adding a large excess of water. In ^{1}H-NMR, the disappearance of the peaks, corresponding to the aromatic protons, was observed. The peak of the methine proton geminal to the amino group coincided with the alkoxy groups of the acrylate.

In order to obtain additional analytical data about the end functional group transformations, Matrix Assisted Laser Desorption Ionization, Time-of-Flight Mass Spectrometry (MALDI-TOFMS) was used. The major peaks observed in the MALDI spectra of azide end-functionalized poly(methyl acrylate) correspond within an error range of +/- 3, to the theoretical mass of the parent product, [87 (CH_3CH(COOMe)-) + nx86 (-CH_2CH(COOMe)-) + 42 (-N_3) + 23 (Na)]$^+$. Small peaks due to the loss of N_2, N_3 and N_3 + CH_3 during MS spectrometry are observed.

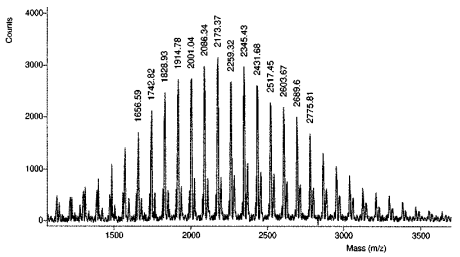

Figure 7 : MALDI-TOF MS spectrum : poly(methyl acrylate) with iminophosphorane end functional groups

For iminophosphorane end-functionalized poly(methyl acrylate) the major and minor peaks correspond both to the parent product ionized with respectively H^+ and Na^+ (Figure 7). The major peaks in the spectrum of amino terminated poly(methyl acrylate) correspond to the parent product, the peaks of lower intensity are caused by the loss of a

methoxygroup and the least intense peaks which are observed between the two others are due to the loss of the amino group.

Conclusion

Well-defined bromo end-functionalized poly(n-butyl acrylate) and poly(methyl acrylate) were prepared by atom transfer radical polymerization. The bromine end groups were quantitatively transformed to azide groups. With the Staudinger reaction, the azide end groups were converted to iminophosphorane end groups which were finally hydrolyzed yielding amino terminated polyacrylate. The transformation of the end groups was observed in IR and ^{1}H-NMR spectrometry. Additional evidence for these reactions was obtained using MALDI-TOFMS which confirmed transformations of end groups.

Acknowledgments

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