Chemistry of the Initiation of Radical Polymerization by Oxygen and Alkylboron Compounds

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Introduction

The initiation of radical chain reactions either in polymer synthesis or in organic synthesis represents an important and well-established area of chemistry.[1,2] The use of organoboron compounds in conjunction with oxygen is one among many methods used to initiate such reactions. This initiation chemistry, which was first developed as a polymerization process,[3,4] has subsequently become of more interest synthetically.[5,6] However, while there is no question about the products and utility of this chemistry in polymer synthesis, the actual radical species that initiate the radical chains are usually not identified.[6−9] Studies of organoborane oxidation chemistry have shown that carbon-based radicals are involved and that alkyl radicals are usually suggested to be the initiating radicals in such chemistry.[10] However, further reaction of these alkyl radicals with oxygen and with alkoxyboranes or peroxyboranes could produce oxygen radicals that might also be capable of initiation of radical chain reactions. This supposition has some support from spin-trapping experiments that have shown alkoxy radicals are produced in the reaction of triethylborane and oxygen.[8] Here we describe simple NMR and chemical studies that show that at least a portion of the radical initiation occurring in polymerizations initiated using esters of alkylboronic and dialkylboronous acids plus oxygen occurs via alkoxy radicals.

Results and Discussion

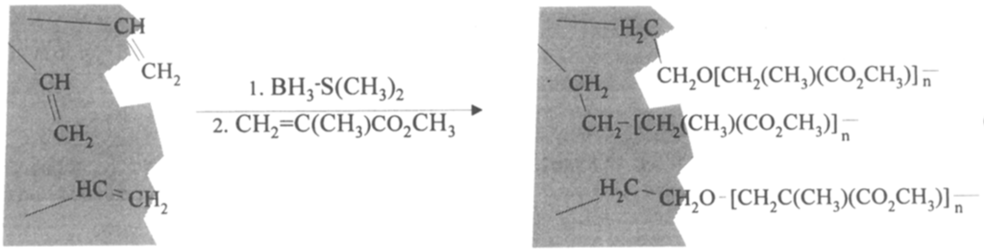
The utility of intermediate alkylboranes in homogeneous graft polymerizations or in heterogeneous grafting onto preformed polymers in the presence of oxygen was the impetus for our initial studies in this area.[11−13] A question that arose in these studies is whether this grafting chemistry proceeds exclusively through an initiation process based on carbon radicals or if oxygen-based radicals were also involved. This question was of interest for both practical and academic reasons. For example, we are pursuing studies of further surface modification of polyolefins first grafted with poly(alkyl methacrylates) using the chemistry in eq 1. In the particular case of polyethylene-*g*-poly(methyl methacrylate) (PE-*g*-PMMA), simple hydrolytic modification of the polyester graft produced changes in both the chemical composition and physical properties of the surface, as summarized in Table 1. It can be seen in Table 1 that treatment of PE-*g*-PMMA with a refluxing ethanol solution containing 0.6 N HCl for 3 h led to an unexpected decrease in the concentration of oxygen at the polymer surface. In this example, XPS spectroscopic analysis showed that the initial polymer surface contained 23 atom % oxygen and this value decreased to ca. 10 atom % oxygen. This was not expected for simple hydrolysis of the ester groups which should have, in fact, increased the atom % of oxygen. In contrast to the results obtained in acidic hydrolysis, alkaline hydrolysis led to little or no change in the atom % of oxygen in the grafted film surface. High-resolution XPS spectroscopy (Figure 1a) further showed that the starting grafted polyethylene contained two types of carbon, one at 292 eV (286 eV, corrected for charging) and one at 288 eV (282 eV, corrected for charging). The former peak is due to the carbonyl carbons of the graft PMMA. After hydrolysis (Figure 1b), the peak intensity for the high binding energy peak in the XPS spectrum of PE-*g*-PMAA was noticeably decreased in size. Both of these data suggest that at least a portion of the grafted chains were attached to the polyethylene via an acid-labile graft site. If oxygen radicals were involved in initiating this graft chemistry, all or a portion of the grafts would have been attached through an ether bond. Such a bond would be acid labile but base stable, and the presence of such a bond qualitatively fits the results shown in Figure 1 and Table 1.

Table 1. XPS and Contact Angle Data for PE-*g*-PMMA Samples before and after Alkaline and Acid Hydrolysis

	XPS spectroscopy[a]			water contact angle[b] (deg)		
sample	O (%)[a]	C (%)	Na (%)	Θ_a	Θ_Y	Θ_r
PE-*g*-PMMA	23	77	<0.5	95	97	*c*
PE-*g*-PMMA hydrolyzed by NaOH/EtoH	26.3	67	6.7	45	45	18
PE-*g*-PMAA after hydrolysis with HCl/EtOH	10.1[c]	89.9[d]	<0.5[d]	94[d]	97[d]	53[d]

[a] The oxygen atom % value for PE-*g*-PMMA varied by ±5%, possibly due to heterogeneities in the extent of grafting across the surface or to different extents of grafting in different experiments. [b] Errors in contact angles are estimated to be ±3°. [c] This value was not measured. [d] Average of two separate experiments with different samples of PE-*g*-PMAA (different PE-*g*-PMMA starting materials).

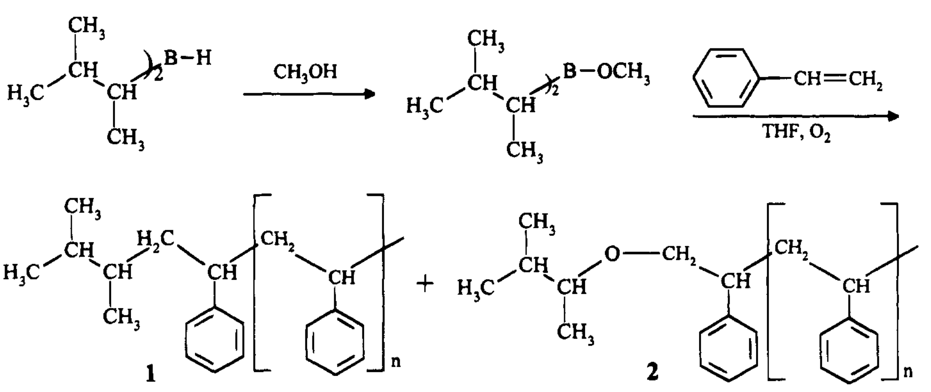
While the miniscule amount of graft produced in modification of polyethylene films was such that it was not possible to isolate and characterize surface grafts from the polyethylene experiment, it is possible to do end group analysis on polymers produced in a homogeneous polymerization. Thus, in an effort to determine if the oxygen-based radicals we hypothesized as intermediates in surface grafts to polyethylene were reason-



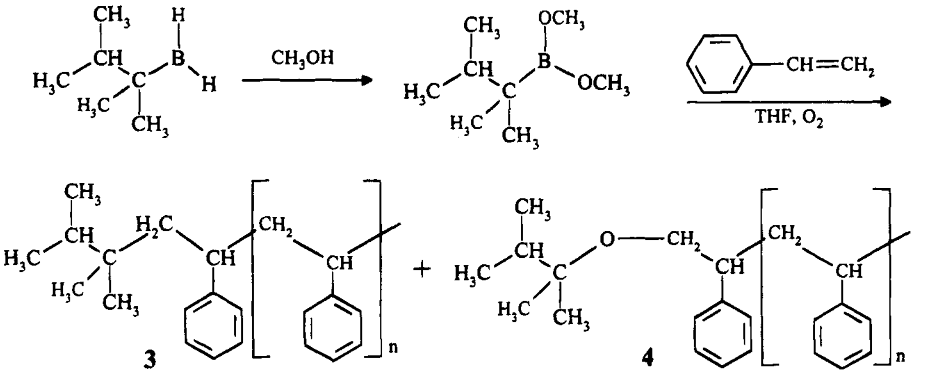
(1)

PE-[H]   PE-*g*-PMMA

0024-9297/95/2228-4756$09.00/0



(2)



(3)

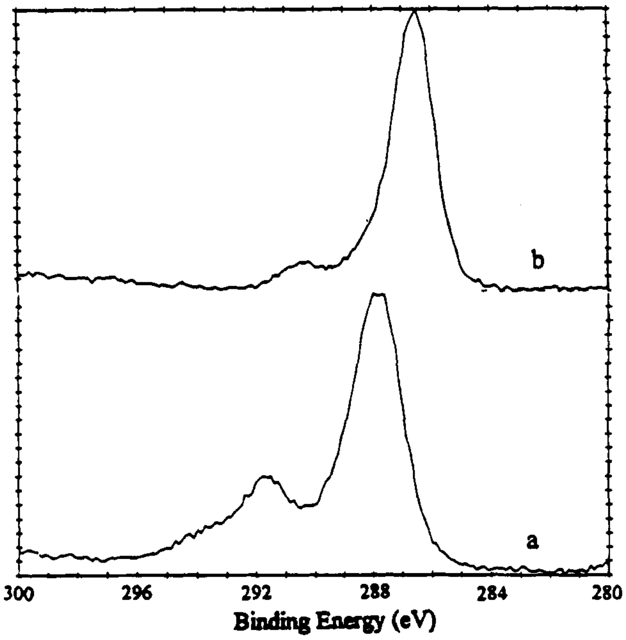


Figure 1. XPS high-resolution spectra showing PE-*g*-PMAA (a) after neutralization of the PE-*g*-PMMA alkaline hydrolysis but before acidolysis and (b) after acidolysis of the PE-*g*-PMAA showing the decrease in the carbonyl carbon intensity.

able, we turned our attention to homogeneous polymerizations initiated by alkylboronic and dialkylboronous acids plus oxygen. The specific polymerizations we chose to examine were styrene polymerizations initiated by oxygen and either dimethyl (1,1,2-trimethylpropyl)boronate or methyl bis(1,2-dimethylpropyl)borinate (eq 2 and 3). These mono- and dialkylboron derivatives resemble the intermediates we believe to be present in heterogeneous grafting onto polyethylene where a large excess of BH_3 is necessarily used in the hydroboration step. The product polystyrene produced in these polymerizations could have either a thexyl (1,1,2-trimethylpropyl) or an isoamyl (1,2-dimethylpropyl) terminal group attached via a carbon–carbon or a carbon–oxygen bond depending on whether an alkyl or alkoxy radical initiated the polymerization. These two possibilities can be distinguished by ^{1}H NMR spectroscopy. Since the polystyrene backbone contains no peaks upfield of δ 1.2, we could examine the methyl peaks of the end groups in the products of eqs 2 and 3. If oxygen radical initiation were involved, we expected to see methyl peaks at about δ 1.1. If carbon radical initiation occurred, we expected to see methyl peaks at about δ 0.9. In fact, methyl signals were present at both δ 1.18 (singlet) and δ 0.93 (multiplet) in a ratio of 7:2. This suggests that both alkoxy and alkyl radicals were involved in initiating the polymerization. Likewise, the methyl region for a polystyrene oligomer initiated by a methyl diisoamylborinate/oxygen mixture contained methyl multiplets at δ 1.15 and 0.88 in a 6:1 ratio. Acidolysis of the dimethyl thexylboronate/oxygen polymerization product largely removed the δ 1.18 peaks due to the ether end groups. This is in accord with the XPS results shown in Table 1 that acidic hydrolysis removed some of the oxygen-containing PMMA graft from an insoluble polyethylene film.

While the polystyrenes produced in eqs 2 and 3 all contained more alkoxy than alkyl end groups, indicating polymerization mainly via alkoxy radicals, we believe the ratio could be sensitive to the monomer used, to the ratio of oxygen/boron initiator, and to the specific chemical structure of the initiator. Irregardless, the NMR studies of the homogeneous system and the XPS and contact angle analyses of the heterogeneous PE-*g*-PMMA film indicate that oxygen-containing radicals and carbon radicals can both play a role in grafting chemistry and polymerization chemistry initiated by alkylborane/oxygen initiation. A mixture of radicals could similarly be involved in radical initiation of synthetic organic reactions using similar alkylborane/oxygen mixtures.

Experimental Section

General Methods. Monomers, borane dimethyl sulfide, hydrogen peroxide, 2,3-dimethyl-2-butene, and 2-methyl-2-butene were obtained from Aldrich Chemical Co. THF was purified by distillation from sodium/benzophenone prior to use. Monomers were purified by distillation and degassed via freeze–thaw before use. The polyethylene used was a linear medium density polymer (Fortiflex J36-25-142) provided by Soltex in the form of a blown film (density of 0.936 g/mL) that contained residual alkene based on the appearance of an absorbance band at 908 cm^{-1} ($-CH{=}CH_2$) on the IR spectrum of the film. Transmission and ATR IR spectra were recorded on a Mattson Galaxy Model 4021 spectrometer. Transmission IR spectra were recorded with a resolution of 2 cm^{-1} with 32 scans, and ATR-IR spectra were recorded at 1 cm^{-1} resolution with 512 scans. ATR-IR spectra were obtained using an MCT detector and a Harrick Scientific Seagul ATR accessory using a hemispherical Zn–Se crystal. Contact angle measurements were made using a Ramè-Hart goniometer using doubly distilled water as the probe liquid and are the arithmetic average of 5–8 measurements. X-ray photoelectron spectroscopy studies were performed on a PHI Model 5500 XPS spectrometer (Mg Kα X-rays, 15 kV, 300 W). The takeoff angle was fixed at 45° unless otherwise noted. ^{1}H NMR spectra were recorded using a 200 MHz Varian Gemini spectrometer in $CDCl_3$.

Preparation of Dimethyl (1,1,2-Trimethylpropyl)boronate (Dimethyl Thexylboronate). A 0.5 M dimethyl thexylboronate solution was prepared in a 100 mL three-necked round-bottomed flask that was equipped with an addition funnel, a septum, and stir bar. The intermediate alkylborane was first prepared by the addition of 2 mL of neat $BH_3{\cdot}S(CH_3)_2$ (10 M) to a solution of 20 mL of 1 M 2,3-dimethyl-2-butene in 20 mL of THF. This borane was then allowed to react with 2 mL of degassed methanol to yield a ca. 0.5 M solution of dimethyl thexylboronate that was used in subsequent polymerizations. A portion of this solution was also used to characterize the dimethyl thexylboronate by ^{1}H NMR and by ^{1}H NMR of an oxidized alcohol product. Removal of THF yielded the crude dimethyl thexylboronate. ^{1}H NMR: δ 0.8 (6H, d), 0.85 (6H, s), 1.8 (1H, m), 3.6 (6H, s). The alcohol produced by alkaline hydrogen peroxide oxidation was also characterized by ^{1}H NMR: δ 0.84 (6H, d), 1.08 (6H, s), 1.55 (2H, m).

Preparation of Methyl Bis(1,2-Dimethylpropyl)borinate (Methyl Diisoamylborinate). A 0.5 M solution of methyl diisoamylborinate was prepared as described above except that 2-methyl-2-butene was substituted for 2,3-dimethyl-2-butene. Treatment of the dialkylborane thus formed with 2 mL of degassed methanol yielded a ca. 0.5 M solution of dimethyl thexylboronate that was used in subsequent polymerizations. A portion of this solution was also used to characterize the methyl diisoamylborinate by ^{1}H NMR and by ^{1}H NMR of an oxidized alcohol product. Removal of THF yielded the crude methyl diisoamylborinate: ^{1}H NMR: δ 0.85 (6H, s), 1.8 (2H, m), 3.7 (3H, s). The alcohol produced by alkaline hydrogen peroxide oxidation was also characterized by ^{1}H NMR; δ 0.82 (6H, d of d), 1.08 (3H, d), 1.55 (1H, m), 1.9 (1H, br s), 3.5 (1H, m).

Preparation of Polystyrene Using Either Dimethyl Thexylboronate or Methyl Diisoamylborinate and Oxygen. Styrene (2 mL) was dissolved in 20 mL of THF in a 50 mL round-bottomed flask equipped with a magnetic stirring bar and sealed with a septum. A 2 mL aliquot of a 0.5 M THF solution of either dimethyl thexylboronate or methyl diisoamylborinate was added using a syringe. Adventitious oxygen present in the anhydrous THF or styrene served as the source of oxygen. After 24 h at 25 °C, the solvent was removed and the residue was dried in vacuum for 24 h. This product was then dissolved in 20 mL of methylene chloride and washed with water. The CH_2Cl_2 was removed by distillation to yield polystyrene which was analyzed by ^{1}H NMR spectroscopy after purification by chromatography. The isolated polymer was obtained in 6–7% yield on the basis of the starting styrene.

Acidolysis of Polystyrene. Polystyrene prepared by the above procedure was hydrolyzed by heating a portion of this isolated polymer in a 0.6 N HCl in ethanol solution at reflux (3 h).

Graft Polymerization To Form PE-*g*-PMMA, Alkaline Hydrolysis of PE-*g*-PMMA, and Acidolysis of PE-*g*-PMMA. The PE-*g*-PMMA film was prepared from medium density polyethylene film by immersing a virgin, extracted PE film in a 1 M THF solution of $BH_3{\cdot}S(CH_3)_2$ for 24 h at 25 °C. The $BH_3{\cdot}S(CH_3)_2$ solution was then removed, and the film was treated with methanol to methanolyze any unreacted B–H bonds. Any excess methanol was removed, and the film was treated with methyl methacrylate. Oxygen could either be added deliberately or be adventitious oxygen present in the methyl methacrylate and/or solvents served to initiate graft polymerization. After 24 h, the film was removed, washed, and extracted with THF in a Soxhlet apparatus for 24 h and finally dried in vacuum. The PMMA graft was then hydrolyzed to form a methacrylic acid graft by hydrolysis with 50 mL of 2 M NaOH in ethanol at reflux (3 h). The product was washed with ethanol twice and dried. An ATR-IR spectrum showed that the ester peak of the graft was gone. Acid hydrolysis of this film was then carried out using 20 mL of a 0.6 N HCl in ethanol solution at reflux (3 h). The product film was analyzed by XPS spectroscopy as noted in the text.

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