Synthesis of alternating vinyl alcohol copolymers

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This paper describes a novel method of preparing two alternating vinyl alcohol copolymers, poly(vinyl alcohol-*co*-ethylene) and poly(vinyl alcohol-*co*-ethylene-*co*-1,4-butadiene). The chemistry involves the ring-opening metathesis polymerization of organoborane monomers, such as 5-cyclooctenyldiethylborane. The borane polymer thus obtained gave upon oxidation a novel polymer structure of poly(vinyl alcohol-*co*-ethylene-*co*-1,4-butadiene) with an alternating molecular structure. The borane polymer could also be further hydroborated prior to the oxidation reaction. This fully hydroborated polymer resulted in an alternating copolymer of poly(vinyl alcohol-*co*-ethylene), which was found to be very thermally stable and began to lose weight only at temperatures above 400°C.

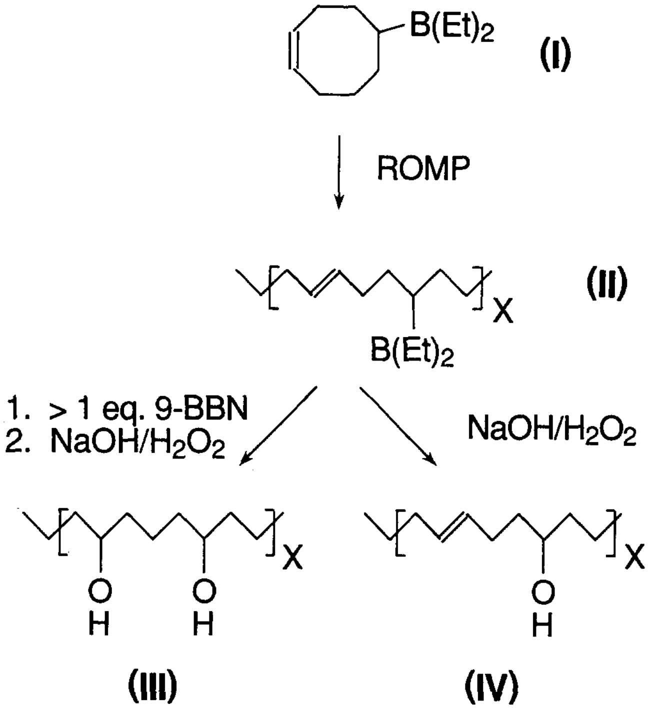
(Keywords: alternating copolymer; poly(vinyl alcohol-*co*-ethylene); poly(vinyl alcohol-*co*-1,4-butadiene); metathesis polymerization; borane monomer; high thermal stability)

INTRODUCTION

Poly(vinyl alcohol) is a useful commercial product for many applications[1], such as food packaging, textile sizing, paper coating, adhesives and emulsifiers. One of the best known properties of poly(vinyl alcohol) is the oxygen barrier[2] under dry conditions. However, its oxygen permeation rate increases by a factor of five orders under high humidity conditions[3]. To reduce the moisture sensitivity, copolymerization with ethylene has been an attractive approach. The optimum composition has been suggested in the range of 30–40 mol% ethylene[4] (commercial Kuyaray EVOH grades contain 32–44 mol% ethylene). In addition, copolymerization has also been used to improve the processibility of poly(vinyl alcohol) homopolymer, which is difficult to fabricate without thermal decomposition.

Poly(vinyl alcohol-*co*-ethylene) is normally prepared by free-radical polymerization[5] of vinyl acetate and ethylene and subsequent hydrolysis or ester interchange reaction. In this process, it is impossible to control the microstructure of the copolymers in an alternating fashion. On the other hand, the synthesis of functional polymers using transition-metal processes has met very limited success[6,7] owing to the reactivity of transition-metal catalysts with a large variety of functional groups. We have recently developed organoborane monomers that can be polymerized by both Ziegler–Natta[8,9] and ring-opening metathesis polymerization[10]. The organoborane polymers thus prepared are quantitatively converted to hydroxyl-containing materials under mild conditions. In our previous paper, we reported the synthesis of a cyclic polymer of poly(*exo*-5-hydroxynorbornene)[10].

In this paper, we extend this new functionalization chemistry to prepare linear functional polymers, particularly two alternating vinyl alcohol copolymers, poly(vinyl alcohol-*co*-ethylene) and poly(vinyl alcohol-*co*-ethylene-*co*-1,4-butadiene). The chemistry involves ring-opening metathesis polymerization (ROMP) of the 5-cyclooctenyldiethylborane monomer (I). The linear polymer (II) obtained in this process has borane groups homogeneously distributed along the polymer chain, as shown below:



Polyborane (II) can be directly oxidized to the alternating copolymer (IV), poly(vinyl alcohol-*co*-ethylene-*co*-1,4-butadiene), or further derivatized by hydroboration before oxidation to give another alternating copolymer, poly(vinyl alcohol-*co*-ethylene) (III).

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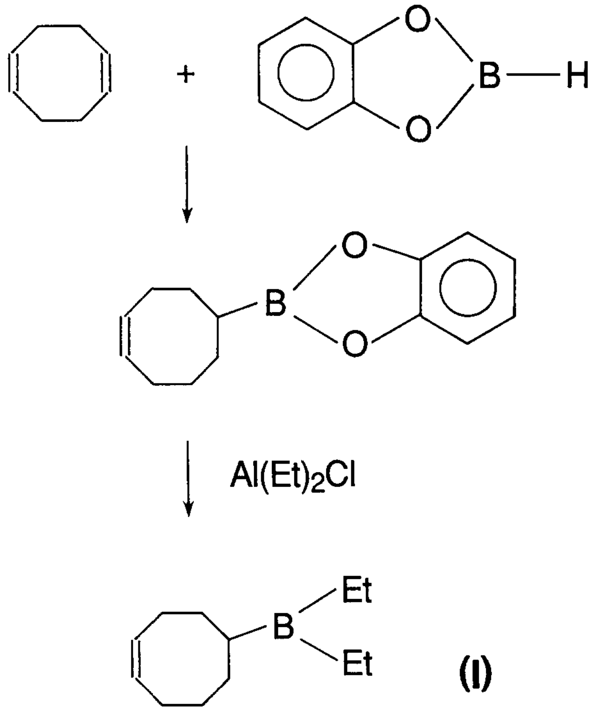
EXPERIMENTAL

Preparation of 5-cyclooctenyldiethylborane

The synthesis of the diethyl derivative was done in two steps as shown below:



(I)

In a Schlenk flask fitted with a Teflon needle valve, 1,5-cyclooctadiene (25 g, 0.231 mol) was mixed with catecholborane (4.3 g, 0.036 mol) and heated to 100°C for about 20 h. This hydroboration reaction was carried out in the absence of solvent, and the unreacted diene was easily recovered by cryogenic distillation in a high-vacuum line. The remaining oil was then dissolved in dry deoxygenated hexane (150 ml), and Et_2AlCl (6.4 g, 0.036 mol) diluted in 100 ml hexane was added to it dropwise with stirring. The reaction was allowed to proceed for about 16 h to give the desirable monomer (I), which could easily be purified by distillation. During the distillation, the hexane was removed cryogenically and the residual oil was subjected to fractional vacuum distillation. The second fraction collected at 50°C (at 0.02 mmHg) yielded about 1.5 g of the required product, to give a 25% yield. Among the various ethylaluminium compounds, diethylaluminium chloride gave the best results, as the dialkoxyaluminium chloride formed was easily separable by filtration. Use of triethylaluminium led to the formation of a viscous reaction mixture, making the isolation of the required product difficult. Triethylaluminium is also more reactive than diethylaluminium chloride, and can undergo an alkyl exchange reaction with the product, trialkylborane, and cause scrambling of the alkyl groups on the borane. A detailed n.m.r. study of such exchange reactions has been done, and is the topic of a forthcoming publication.

Polymerization and oxidation reactions

Polymerization was carried out in a dry-box by mixing 5-cyclooctenyldiethylborane (500 mg, 2.81 mmol) and $W(=CHBu^t)(NAr)[OCMe(CF_3)_2]_2$ (11 mg, 0.014 mmol) in 1 ml of toluene. The reaction was instantaneous, causing the solution to gel. After 2 h stirring, the polymerization was terminated by the addition of an excess of 2-propanol. The precipitated polyborane was washed thoroughly and redissolved in about 10 ml of tetrahydrofuran (THF). The THF solution was put in a 50 ml Schlenk flask and removed from the dry-box. A 6 N NaOH solution (0.61 ml, 3.66 mmol) was degassed by bubbling dry argon through it, and was added to the polymer solution under a flow of argon. Then 30% H_2O_2 solution (1.25 ml, 10.9 mol) was added dropwise to the polymer solution, which was cooled in an ice–water bath. After the addition was completed, the solution was heated in an oil bath at 40–50°C for 12–16 h. The polymer was precipitated in water, washed and redissolved in THF. A small amount of insoluble material was removed by centrifugation and the clear solution was precipitated in water. The polymer was dried in a vacuum oven at 50°C. The yield after oxidation was 210 mg, which corresponds to a 60% yield.

Hydroboration of the polyborane

The polymerization was carried out as described above. After the polymerization, a few drops of 2-propanol were added to cause termination and about 10 ml of THF was used to dissolve the gel. Then 9-borabicyclo[3.3.1]nonane (9-BBN) in slight excess was added to the polymer solution and allowed to react for about 16 h. The oxidation and purification of the polymer were carried out similarly to those described above. A smaller mole ratio of 9-BBN was used to effect a smaller extent of hydroboration.

RESULTS AND DISCUSSION

The monomer (I) was polymerized using a Lewis-acid-free metathesis catalyst, $W(=CHBu^t)(NAr)[OCMe(CF_3)_2]_2$, provided by K. B. Wagener. Polymerization occurred very rapidly and the polymer (II) formed was oxidized using alkaline H_2O_2 to give poly(5-hydroxycyclooctenomer) (IV), which has a novel molecular structure as a copolymer of vinyl alcohol, ethylene and 1,4-butadiene, leading to an alternating microstructure. The unique feature of this ring-opening polymerization lies in the fact that the arrangement of the comonomer units, i.e. vinyl alcohol, ethylene and 1,4-butadiene, on the backbone is mostly precontrolled in the starting cyclic monomer structure (I). Only a small variance in the arrangement occurs due to the presence of various head-to-head, head-to-tail and tail-to-tail sequences. This polymer (IV) is very soluble in many organic solvents, such as THF and chloroform. *Figure 1a* shows the ^1H n.m.r. spectrum of polymer (IV); the relative integrated intensities of the vinylic (5.5 ppm) and allylic (~2.05 ppm) protons are in accordance with the expected structure. The polymer was found to contain mainly *trans* double bonds, as can be seen from its ^{13}C n.m.r. spectrum shown in *Figure 2a*. Based on the relative intensity of the respective olefinic carbons, the *trans* content was found to be about 80%.

The borane polymer (II) was further modified by hydroboration with 9-BBN prior to oxidation. By controlling the stoichiometry of the hydroborating agent, one could get either partially or completely hydroborated polymers, which upon oxidation give poly(alcohol)s. The extent of functionalization was calculated from the relative intensity of the vinylic or allylic protons.

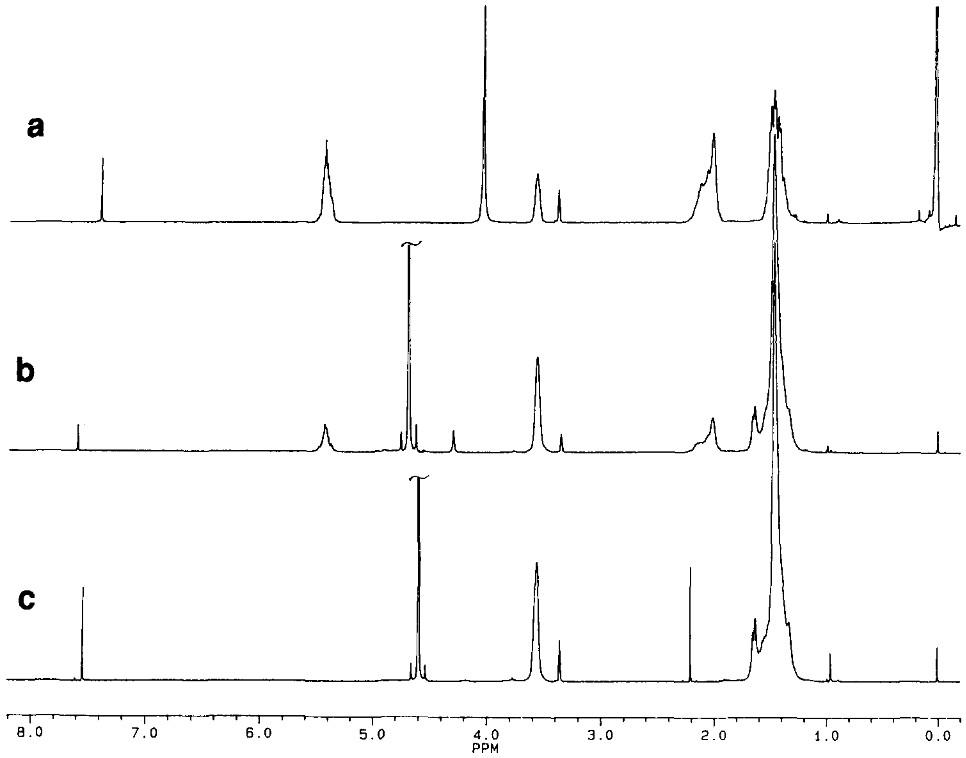


Figure 1 ^{1}H n.m.r. spectra of alternating copolymers: (a) poly(vinyl alcohol-*co*-ethylene-*co*-1,4-butadiene); (b) partially hydroborated copolymer; (c) poly(vinyl alcohol-*co*-ethylene)

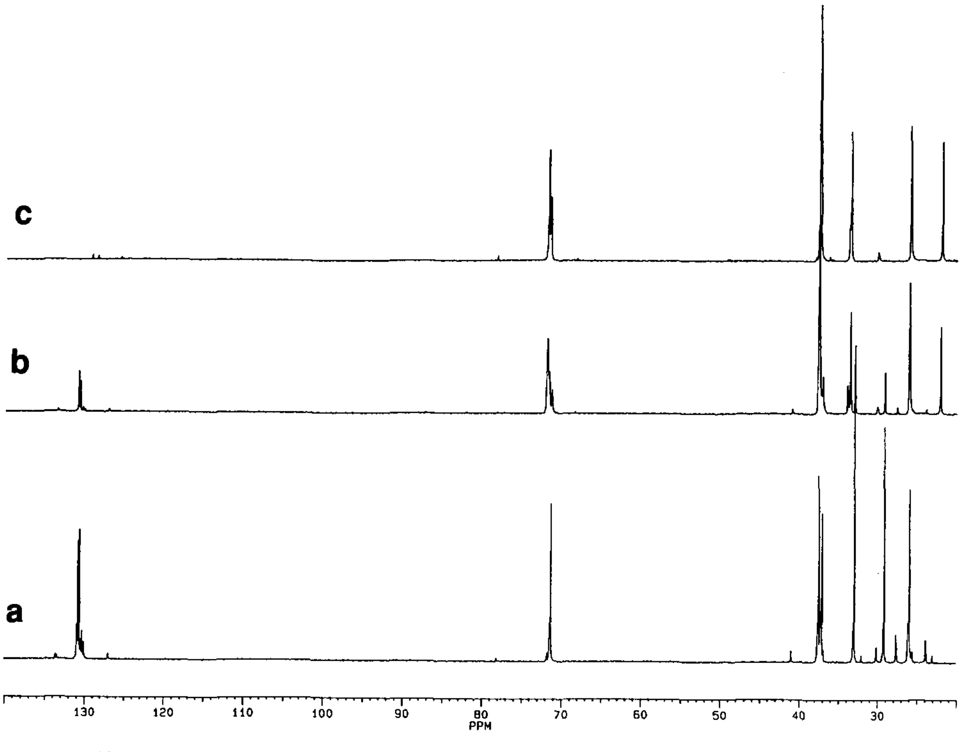


Figure 2 ^{13}C n.m.r. spectra of alternating copolymers: (a) poly(vinyl alcohol-*co*-ethylene-*co*-1,4-butadiene); (b) partially hydroborated polymer; (c) poly(vinyl alcohol-*co*-ethylene)

One example is shown in *Figure 1b*. The 75% hydroborated compound shows intensity reduction at both peaks, $\delta = 5.5$ ppm and $\delta \simeq 2.05$ ppm, to about a quarter of the original sample. The same results are also observed in the ^{13}C n.m.r. spectrum. *Figure 2b* shows a significant reduction in both vinylic ($\delta = 131$ ppm) and allylic ($\delta = 29$ ppm) carbon peaks. With a stoichiometric amount of hydroborating agent to double bonds, one can get completely hydroborated polymer, which upon oxidation gives poly(vinyl alcohol-*co*-ethylene). This polymer has exact 50/50 copolymer composition, with alternating microstructure (III). The ^{1}H n.m.r. spectrum of polymer (III) is shown in *Figure 1c*. The complete absence of vinylic protons at $\delta = 5.4$ ppm is expected in

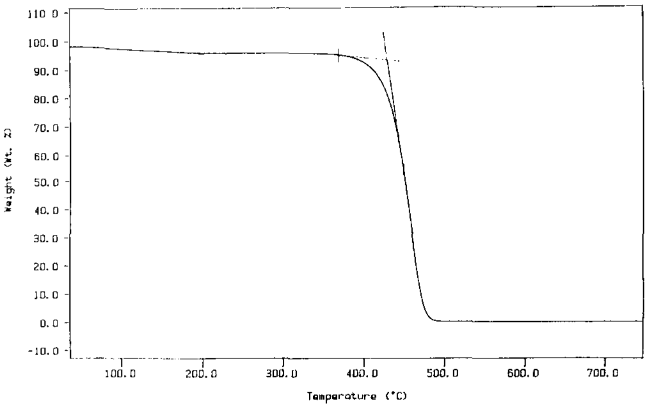


Figure 3 T.g.a. curve of poly(vinyl alcohol-*co*-ethylene)

polymer (III). The detailed structural information is revealed in the ^{13}C n.m.r. spectrum (*Figure 2c*). In addition to the complete disappearance of chemical shifts corresponding to vinylic and allylic carbons, the chemical shift around 71 ppm is split into two peaks, which indicates two types of secondary alcohols in polymer (III). This may result from the hydroboration reaction, which involves two carbons in the double bond, both of them available to form a C–B bond.

The alternating copolymer of poly(vinyl alcohol-*co*-ethylene) was soluble only in mixed solvents such as THF/methanol and chloroform/methanol. This polymer (III) after acetylation was soluble in pure THF, and hence its molecular weight after acetylation was determined by g.p.c. using THF as the solvent. The molecular weight was found to be 122 000, with a polydispersity of 2.8. The molecular weight was quite high for this type of reaction. It is interesting to note the advantages of borane monomer, which is not only stable to the metathesis catalyst but also of good solubility in hydrocarbon solvents. All borane-containing materials, including the starting monomer and growing polymer, are soluble in solution, which offers the optimum condition for preparing high-molecular-weight polymer. In addition, the borane polymers are easily converted to a variety of other functionalities under mild conditions[11,12].

The thermal properties of both alternating copolymers were examined by d.s.c. and t.g.a. techniques. The glass transition temperature of polymer (IV) was about 11°C and increased to about 45°C upon complete functionalization to give poly(vinyl alcohol-*co*-ethylene) (III). The thermal stability of polymer (III) was found to be significantly higher than that of poly(vinyl alcohol), which decomposed at temperatures below 250°C[13]. The t.g.a. curve of polymer (III) is shown in *Figure 3*. This polymer begins to lose weight near 400°C. The higher thermal stability is noteworthy, as this polymer has a very similar structure to that of poly(vinyl alcohol) and yet degrades at much higher temperatures.

CONCLUSIONS

In conclusion, we have demonstrated a novel route to the synthesis of poly(5-hydroxyoctenomer), an alternating copolymer of vinyl alcohol, ethylene and 1,4-butadiene. Further use of hydroboration chemistry allows us to access an alternating copolymer of vinyl alcohol and ethylene. The glass transition temperatures of polymers increase with the hydroxyl content. The most interesting feature is the greater thermal stability of polymer (III) as compared to a similar analogue such as poly(vinyl alcohol). Further exploration of the utilization of borane monomers and ring-opening metathesis polymerization can lead to a variety of new and interesting functional polymers with regular molecular structures.

ACKNOWLEDGEMENTS

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