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Well-Defined Ethylene–Vinyl Alcohol Copolymers via Hydroboration: Control of Composition and Distribution of the Hydroxyl Groups on the Polymer Backbone

S. Ramakrishnan*

Corporate Research Laboratory, Exxon Research and Engineering Company, Route 22 East, Clinton Township, Annandale, New Jersey 08801

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ABSTRACT: Cyclic olefins having different ring sizes were polymerized by ring-opening metathesis polymerization to give polyalkenylenes that have double bonds separated by varying numbers of methylene units. Upon hydroboration followed by oxidation, these polyalkenylenes yielded ethylene–vinyl alcohol copolymers whose vinyl alcohol content varied from 16 to 50 mol %. The ^{1}H NMR and ^{13}C NMR spectra of these copolymers confirmed their structure and indicated that the hydroboration–oxidation reaction sequence was complete. Because of the absence of branching in these copolymers, they represent copolymers of linear polyethylene and vinyl alcohol. This is unlike the commercially manufactured ethylene–vinyl alcohol copolymers, which have branching. The melting points of these copolymers were found to go through a minimum at a composition of ~40 mol % vinyl alcohol. At higher ethylene content the melting point approaches that of linear high-density polyethylene. Since this approach allows the complete control of both the composition and the spacing between the hydroxyl groups on the polymer backbone, these copolymers serve as excellent models for understanding the structure–property relationship in such systems.

Introduction

Ethylene–vinyl alcohol copolymers have excellent barrier properties and have found extensive application in food packaging.[1] In recent years, they have also been studied as candidates for biomedical and pharmaceutical applications.[2] They are prepared commercially by a free-radical process from ethylene and vinyl acetate. Saponification of the acetate groups after polymerization yields the required ethylene–vinyl alcohol (EVAL) copolymers. Owing the the free-radical nature of the polymerization, the resulting copolymers possess a certain degree of branching and therefore can be considered to be copolymers of low-density polyethylene (LDPE) and vinyl alcohol.

Control of both composition and distribution of functional groups in copolymers is important for the complete understanding of their structure–property relationships. Although the composition of the copolymers can be well controlled in some cases, the uniformity of the monomer distribution and the spacing between them on individual polymer chains are not easily achieved. Depending on the reactivity ratios of the two monomers, various distributions can result. Furthermore, the distribution within the chain and the compositional uniformity of different polymer molecules in the bulk sample can vary with the conversion. Therefore, development of techniques that allow the control of these different parameters would greatly benefit our fundamental understanding of polymer properties.

It was demonstrated in our laboratory that the hydroboration–oxidation sequence can be used very effectively to convert double bonds in polymers into hydroxyl groups.[3] The advantage of this method lies in the fact that the hydroboration and oxidation reactions can be carried out to completion in a homogeneous manner. Ring-opening metathesis polymerization (ROMP) of cycloolefins having different ring sizes was done to give polyalkenylenes.[4] Polyalkenylenes thus prepared have double bonds along their backbone that are separated by differing numbers of methylene units and can be considered copolymers of ethylene and acetylene. Hydroboration–oxidation of these polyalkenylenes resulted in ethylene–vinyl alcohol copolymers. In this article, we demonstrate the use of this hydroboration–oxidation sequence to synthesize ethylene–vinyl alcohol copolymers with complete control over both the composition and the placement of the hydroxyl groups in the polymer.

Experimental Methods

Materials. Cycloheptene, 1,5-cylooctadiene, and cyclododecene were purchased from Aldrich Chemical Co. and cyclopentene was purchased from Wiley Organics. All the cycloolefins were purified by distillation over sodium metal and stored under argon. Toluene and tetrahydrofuran (THF) were distilled over sodium benzophenone ketyl, chlorobenzene was distilled over P_2O_5, and they were stored under argon. WCl_6 (Aldrich) was used directly, while Me_4Sn (Aldrich) was purified by distillation over CaH_2. W(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$ was kindly provided to us by Professors K. B. Wagener and J. Boncella. 9-Borabicyclo[3,3,1]nonane (9-BBN) was purchased from Aldrich and used directly. Polyoctenylene (available under the trade name Vestenamer 8012) was gifted to us by Hüls America.

Polymerization of Cycloolefins. Typically, WCl_6 (monomer/W = 200) was weighed into a Schlenk tube in the drybox (Vacuum Atmospheres) and the required amount (to result in a 3 M monomer solution) of chlorobenzene was added to it by syringe. After the resultant mixture was stirred for ~30 min, Me_4Sn (Sn/W = 2) was added by microsyringe. The catalyst mixture was allowed to age for 5 min at room temperature before the required amount of the cycloolefin was added. The reaction was allowed to proceed for ~2 h and was terminated by addition of an excess of methanol. The polymer was redissolved in THF, precipitated in methanol, and dried in a vacuum oven. 1,5-Cyclooctadiene was polymerized similarly, the only difference being that a higher monomer concentration of 4.5 M was used. Cycloheptene and cyclododecene were polymerized by using W(CH-*t*-Bu)(NAr)(OCMe[$CF_3]_2)_2$ as the polymerization catalyst. A much higher monomer/catalyst ratio of 500 was used in this case and the polymerization was carried out in toluene using a 2 M monomer solution. The polymer yields are given in Table I. The polyalkenylene samples were stored in the drybox to prevent oxidative degradation.

Hydroboration and Oxidation. A 1–2 wt % solution of the polyalkenylenes in THF was put in a Schlenk flask with a Teflon

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* Current address: Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India.

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Table I

polymer	catalyst	% yield	M_n ($\times10^{-3}$)	T_m, °C	% trans	M_w/M_n
polybutenylene C4	WCl_6/Me_4Sn	58	159	*a*	17.7	1.62
polypentenylene C5	WCl_6/Me_4Sn	46	273	8.4	82	2.14
polyheptenylene C7	*b*	80	91	45.9	81	1.56
polyoctenylene[c] C8			86	49.1	73	1.64
polydodecenylene C12	*b*	84	5.5	79.8	87	4.02

[a] Amorphous sample. [b] W(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2$]$_2$. [c] Commercial sample from Hüls America under the trade name Vestenamer 8012.

needle valve closure, and 9-BBN (1.3 mol excess) was added to it. The closed container was then placed in an oil bath that was maintained at a temperature of 50–70 °C for a period of 16–24 h. The polymer solution was then cooled in an ice-water bath. The required amount of aqueous 6 N NaOH solution (1.3 mol/mol of borane) was placed in an addition funnel, degassed by bubbling argon, and added dropwise to the stirred polymer solution. A 30 wt % aqueous solution of H_2O_2 (3.9 mol/mol of borane) was degassed similarly and then added dropwise to the polymer solution. The solution was allowed to warm to room temperature and was placed in an oil bath maintained at 40–50 °C for 16–24 h. During the oxidation, the outlet of the flask was connected to a bubbler under argon. The polymer was isolated by pouring the solution into water and was washed several times with water. It was redissolved in a THF–methanol mixture, precipitated in water, washed several times with acetone, and dried in a vacuum oven at 50–60 °C. The yield in all cases was greater than 95%.

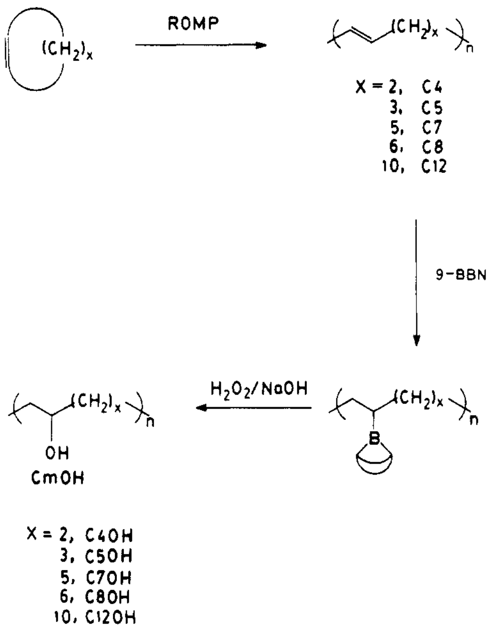
Instrumentation. The NMR spectra were recorded on a Bruker AM-360 spectrometer. A distortionless enhancement by polarization transfer (DEPT) pulse sequence using a nutation angle of 45° rendered the complete carbon-13 spectrum in all cases, as the polymer did not have any quaternary carbons that were not observable by this pulse sequence. This allowed the spectra to be recorded in a much shorter time because of the higher signal-to-noise ratio achievable with this sequence. Since the relative intensities of only the methylene carbons were used for determination of the diol composition, the DEPT pulse sequence was considered adequate for the analysis. All the ^1H NMR spectra were recorded with a delay time of 30 s. This was necessary to ensure complete relaxation of the different protons and allowed quantitative determination of the copolymer composition. The GPC chromatograms were obtained by using a Waters 600E delivery system that was connected to a Waters 410 refractive index detector. A series of three Ultrastyragel columns with pore sizes of 10^3, 10^4, and 10^6 Å was used to effect the separation. The molecular weights were determined by use of polystyrene as the calibration standard. The DSC measurements were performed on a Perkin-Elmer DSC-2 instrument.

Results and Discussion

The general approach for the synthesis of the ethylene–vinyl alcohol copolymers is outlined in Scheme I.

A series of cycloolefins with ring sizes ranging from 5 to 12 was polymerized by ring-opening metathesis reaction to give the corresponding polyalkenylenes. 1,5-Cyclooctadiene (1,5-COD) and cyclopentene were polymerized by use of standard catalyst, WCl_6–Me_4Sn, to give polybutenylene [or poly(1,4-butadiene)] and polypentylene, respectively. Cycloheptene and cyclododecene were polymerized by use of a highly active tungsten carbene, W(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2$]$_2$.[5] The yields in the latter cases were significantly higher. The microstructure of the polymers depended on the particular catalyst/monomer combination. The trans content in the polymers was determined from the relative intensities of the trans and cis olefinic carbon peaks located at 130.3 and 129.8 ppm, respectively. Polybutenylene, prepared from *cis,cis*-1,5-COD, gave a high-cis polymer unlike the remaining cases because only one of the double bonds in the monomer was involved in the polymerization; the other one being cis in the monomer remains so in the polymer.[6] The molecular weights of the polymers were determined by GPC (versus polystyrene standard) and were found to lie between 90 000 and 300 000, except in the case of polydodecenylene, which had a much lower molecular weight of 5500. The considerably lower molecular weight of polydodecenylene may render the comparison of the properties of C12OH with remaining polymers less straightforward. The yields of the various polymers, their isomeric composition, and their molecular weights are listed in Table I.

Scheme I



Structural Analysis. The ^1H NMR spectra of the polyalkenylenes are shown in Figure 1. The relative intensity of the olefinic peak at 5.3 ppm is in good agreement with the expected degree of unsaturation in all cases.[7] In order to obtain quantitative results, a 30-s delay time was used during acquisition. It was previously noticed that double-bond isomerization can occur during polymerization under certain conditions.[8] In order to demonstrate the absence of any such isomerization, the ^{13}C NMR spectra of all the polymers were recorded and are shown in Figure 2. In all cases the peaks can be assigned to the expected structure and their chemical shifts match the reported values.[8] Isomerized segments are demonstrably absent in the cases of C4, C5, and C7 polymers, but their absence cannot be proven unequivocally from the spectra in the C8 and C12 cases. This is because small shifts in double bonds due to isomerization cause only very little shifts in the position of the different carbon peaks, when the number of methylenes between the double bonds is greater than five. However, on the basis of the behavior of the C4–C7 polymers, it can be inferred that no isomerization occurs in the latter cases as well. This confirmation is critical to the further analysis of the EVAL copolymer properties. The accuracy of the spacing between the hydroxyl groups in the copolymers presupposes the absence of any such isomerization.

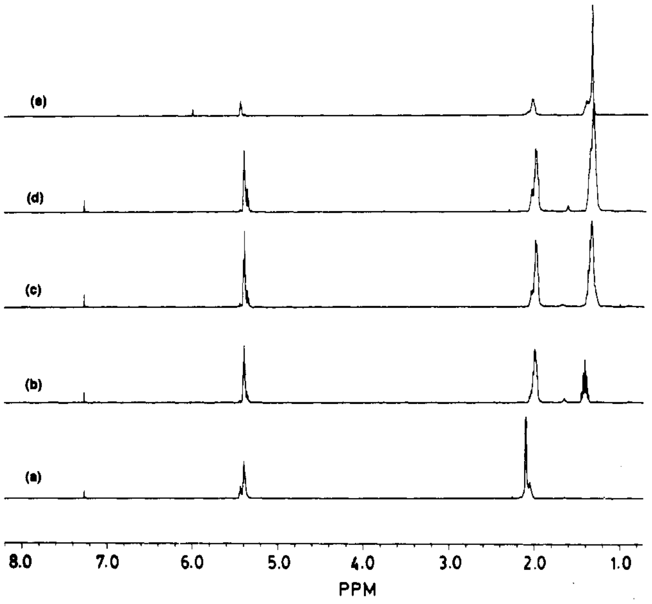


Figure 1. ^1H NMR spectra of polyalkenylenes. (a) Polybutenylene, (b) polypentenylene, (c) polyheptenylene, (d) polyoctenylene, (e) polydodecenylene.

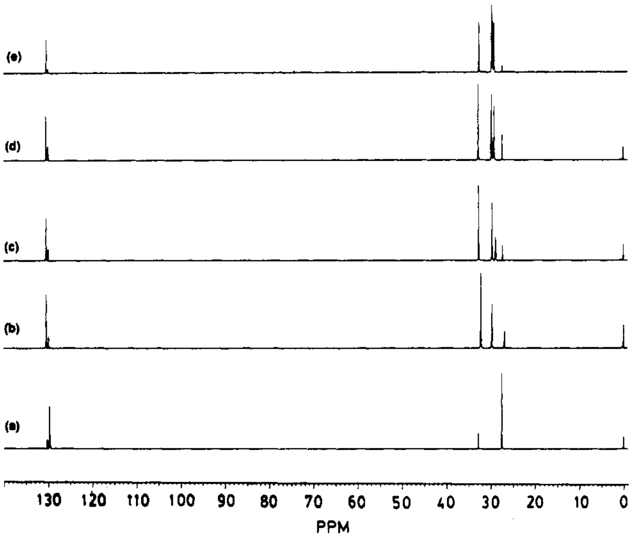


Figure 2. ^{13}C NMR spectra of polyalkenylenes. (a) Polybutenylene, (b) polypentenylene, (c) polyheptenylene, (d) polyoctenylene, (e) polydodecenylene.

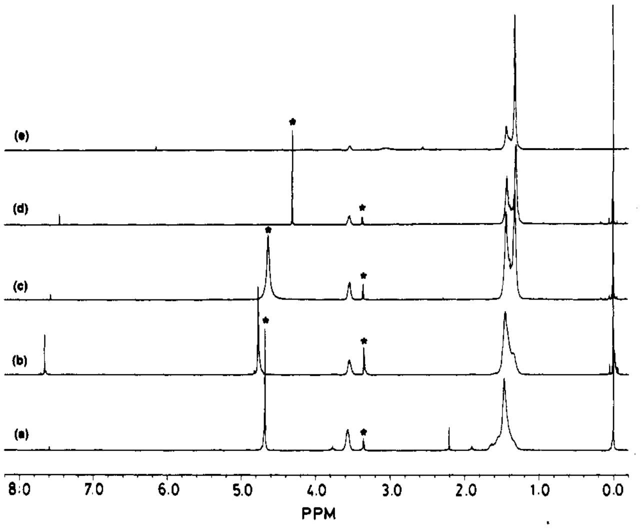


Figure 3. ^1H NMR spectra of C*m*OH copolymers. (a) C4OH, (b) C5OH, (c) C7OH, (d) C8OH, (e) C12OH.

Table II

polymer	mol % vinyl alcohol obsd[a]	mol % vinyl alcohol theor
C4OH	48.7	50
C5OH	40	40
C7OH	27.9	28.6
C8OH	25	25
C12OH	16	16.7

[a] Obtained from the relative intensity of the methine proton (3.57 ppm) in the ^1H NMR spectrum.

Hydroboration of the polyalkenylenes was carried out using 9-BBN. To accomplish complete hydroboration, we used an excess of the reagent. The reaction temperature used was between 50 and 70 °C. In the C12 case, the higher temperature was used to ensure that the polymer was completely soluble in the beginning. The C12 polymer exhibited a cloud point temperature below which it came out of solution. This behavior is to be expected as the polymer becomes more like polyethylene. Typically, a 1–2 wt % solution of the polymer in THF was used for the hydroboration and the reaction was carried out for 16–24 h. Oxidation of the hydroborated samples was carried out directly after hydroboration, as described previously.[9] The polyalcohols obtained are labeled C*m*OH, where *m* is the number of carbon atoms in the polymer repeat unit (Scheme I). The solubility of the polymers greatly depended on the hydroxyl content. The polymers were soluble in solvents such as THF and chloroform, only in the presence of varying amounts of polar cosolvents like methanol, DMSO, and DMF. The amount of the polar component required increased with the hydroxyl content in the copolymers. The C12OH sample also exhibits a cloud point temperature below which it is insoluble in any solvent mixture. Similarly, C8OH gels slowly upon being kept at room temperature for extended periods of time. This gelation is completely reversible and the polymer redissolves upon heating. The existence of a cloud point temperature is consistent with the fact that the polymer begins to exhibit characteristics of polyethylene with increasing ethylene content. As the process of hydroboration–oxidation was carried out under mild conditions, it is unlikely to cause any degradation of the polymer. In the case of C4OH, the GPC profiles of the parent polymer and the functionalized polymer were compared. The M_n value increased from 95 000 to 145 000 upon hydroxylation followed by acetylation. The GPC profile after functionalization was, however, broader, which may be due to some kind of interaction of the functional group with the column.

The ^1H NMR spectra of the C*m*OH copolymers are shown in Figure 3. The spectra were recorded in a mixture of $CDCl_3$ and CD_3OD. The peak at 3.57 ppm represents the methine proton, C*H*OH. The relative intensity of this peak was used to determine the copolymer composition. The mole percent of vinyl alcohol calculated thus is in good agreement with the expected values (Table II), indicating the completeness of the hydroboration–oxidation sequence. The completeness of the reaction is also confirmed by the absence of vinyl protons (5.3 ppm) in all the cases. The maximum amount of vinyl alcohol that can be incorporated by this method is 50 mol % (in C4OH), which is obtained from poly(1,4-butadiene). The C4OH copolymer represents an alternating copolymer of ethylene and vinyl alcohol.

Because of the presence of two sites on the double bond for hydroboration, three types of diol segments are always generated. Thus, C*m*OH would generate 1,*m*-, 1,(*m* + 1)-,

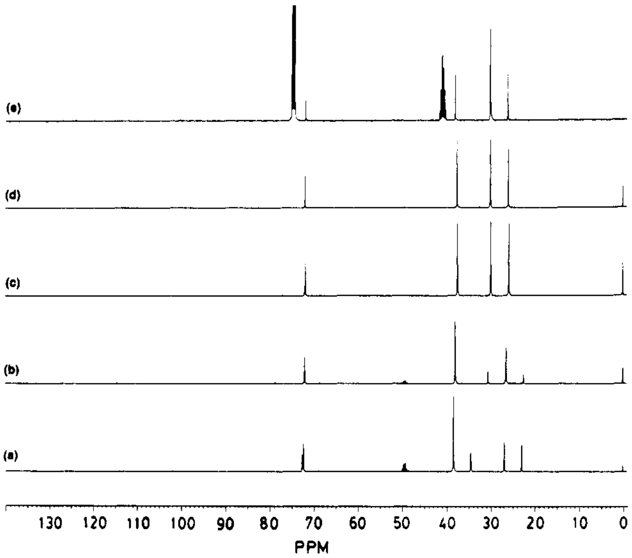


Figure 4. ^{13}C NMR spectra of C*m*OH copolymers. (a) C4OH, (b) C5OH, (c) C7OH, (d) C8OH, (e) C12OH.

and 1,(*m* + 2)-diols. In the case of a statistically random hydroboration, one would expect these diols to be present in the ratio 1:2:1, respectively. The ^1H NMR spectra of the polymers show only one type of methine proton in all cases, including the copolymers with the highest vinyl alcohol content. The presence of these different diol segments in the copolymers, however, can be proved and quantified by ^{13}C NMR, as will be shown later. On the other hand, the commercial EVAL copolymers with a similar composition exhibit three kinds of methine protons because of the presence of smaller diol (1,3-diols) segments and the different diad sequences that can result.[10]

A number of detailed ^{13}C NMR studies of the microstructure of the commercial EVAL copolymers have been carried out.[11] The presence of various diol segments and their diad combinations has been established. Studies have also indicated the presence of branching in these copolymers, the amounts of which have also been quantified.[12] As in the case of the proton spectra, the carbon-13 spectra of the commercial EVAL copolymers also show the presence of different methine carbons corresponding to the different environments that are present in them. On the other hand, the ^{13}C NMR spectra (Figure 4) of the C*m*OH copolymers are relatively simple and show the presence of only one kind of methine carbon. In the case of C4OH, some fine structure is observed due to the chemical shift differences between the methine carbons corresponding to the 1,4-, 1,5- and 1,6-diols.[13] In the other C*m*OH polymers, the difference in chemical shifts between the methine carbons belonging to the different diol segments is very small, and therefore, only a single peak is observed. The various peaks were easily assigned from the expected shifts due to secondary alcohol groups and from group additivity rules.[13] The concentration of the three different diol segments in C4OH and C5OH can be calculated from the relative intensities of the peaks that arise specifically due to one of these diol units. Since the comparison of the relative intensities is restricted only to the methylene carbons, the DEPT pulse sequence should render accurate results. The 1,4- and 1,5-diol segments exhibit very characteristic peaks.[13] The C_γ peak (22.3 ppm) in the 1,5-diol is shifted far upfield by virtue of being γ to both the hydroxyl groups, as compared to the γ-carbon peak of a 1,6 or longer diol segment (26.7 ppm), which is γ to only one hydroxyl groups. Thus, the concentration of the three diols in C4OH and C5OH, both of which exhibit this C_γ peak, can be calculated from the relative intensity of this peak. The calculation indicates that the intensity is approximately in the ratio 1:2:1, as expected (Table III). In the case of the higher C*m*OH copolymers there are no peaks that specifically represent either of the three diols, and therefore, the calculation of the relative population of the different diol segments is not possible. However, the absence of the short diol segments (smaller than 1,6-diol) in the case of C7OH, C8OH, and C12OH is apparent from the absence of peaks due to such segments. On the basis of the predictable behavior of C4OH and C5OH and the cleanliness of the chemistry, it can be safely concluded that the other C*m*OH copolymers also possess only the three expected diol segments, namely, 1,*m*-, 1,(*m* + 1)-, and 1,(*m* + 2)-diols in the ratio 1:2:1.

Table III

polymer	mol %			
	1,4-diol	1,5-diol	1,6-diol	1,7-diol
C4OH	24.6	47.7	25.7	0
C5OH	0	24.17	49.07	26.8

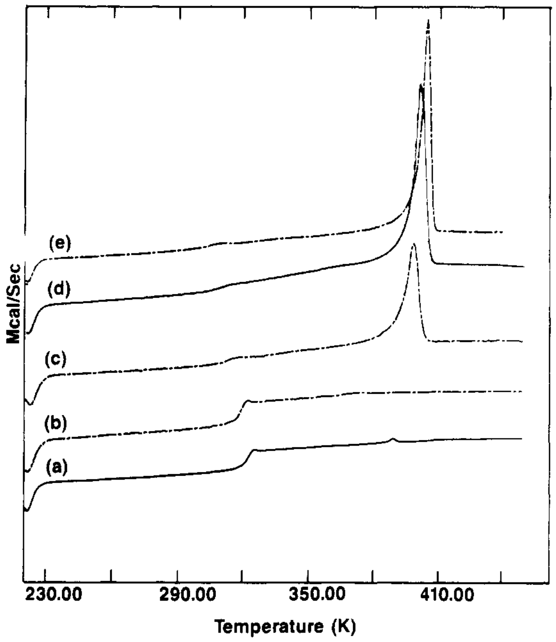


Figure 5. DSC scans of quenched C*m*OH samples. (a) C4OH, (b) C5OH, (c) C7OH, (d) C8OH, (e) C12OH.

Thermal Analysis. The thermal behavior of the copolymers was studied by DSC. In order to establish similar thermal history, the samples were first heated to 450 K and quenched rapidly to 220 K. Prior to quenching, the samples were maintained at 450 K until no further thermal activity was noticed. Samples treated in this fashion were then scanned at the rate of 20°/min. Figure 5 shows the DSC scans of the polymer samples obtained in this manner. It was confirmed that the DSC thermograms of subsequent scans of the quenched samples were completely reproducible. From these scans, it is apparent that as the content of vinyl alcohol in the copolymers decreases (higher values of *m*), the copolymers crystallize much more readily. Even upon rapid quenching, C7OH and higher copolymers retain a high degree of crystallinity, as indicated by the presence of a large melting transition. The glass transition temperature of C12OH appears as a very weak transition, indicating its highly crystalline nature. The enthalpies involved with the melting transition (Table IV) also increase with the ethylene content in the copolymers. Quenched samples of C4OH and C5OH, on the other hand, are almost completely amorphous and

Table IV

polymer	mole % VA	T_g, °C	T_m, °C	ΔH,[a] cal/g
C2OH	100	85[b]	240[b]	
C4OH	48.7	48.5	113.6	8.64
C5OH	40	45.4	102.6	3.66
C7OH	27.9	37.8	125.2	14.16
C8OH	25	35.1	128	15.96
C12OH	16	31.6	135	22.08
HDPE	0	-125[b]	137.5[b]	

[a] Values obtained for annealed samples. [b] Values taken from: *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975.

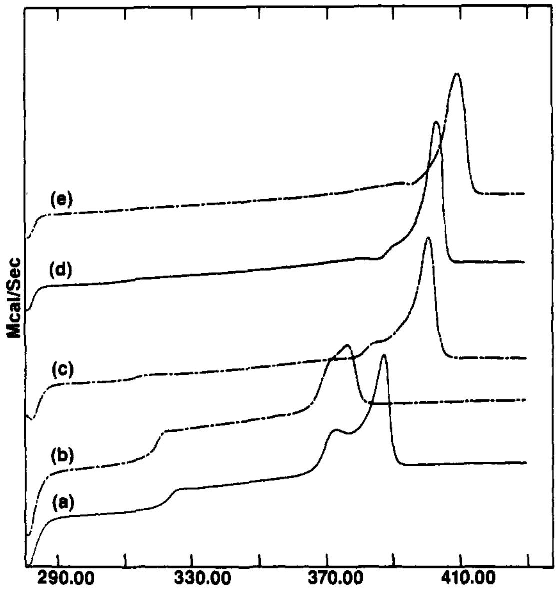


Figure 6. DSC scans of annealed C*m*OH samples. (a) C4OH, (b) C5OH, (c) C7OH, (d) C8OH, (e) C12OH.

exhibit a very large change in the heat capacity upon going through the glass transition temperature.

In order to determine the melting point of the amorphous polymer samples, C4OH and C5OH samples were annealed at about 30–40 °C above their glass transition temperature for a period of 16–24 h. The DSC scans of the annealed samples are shown in Figure 6. The glass transition temperature (T_g) and melting temperatures (T_m) of the different C*m*OH copolymers are listed in Table IV along with their enthalpies of melting. The percent crystallinityof the copolymers was not established; therefore, the enthalpies do not reflect differences in the nature of the crystal lattice.

In order to obtain amorphous samples of the copolymers that crystallize rapidly, attempts were made to quench molten samples in liquid nitrogen. Samples were heated in air to ~50 °C above their melting temperature in a hot press and quenched by rapid immersion into liquid nitrogen. The DSC scans of C7OH and C8OH samples treated in this manner are shown in Figure 7. An interesting behavior is noticed in these samples. As the sample is taken through its glass transition temperature, it attains enough chain mobility to allow its reorganization and cause crystallization. The exothermic peak observed as the sample passes through its T_g is the result of this crystallization process. The size of this exothermic peak as compared to the melting peak gives a qualitative indication of the percent amorphous region initially present in these quenched samples. As expected, the C8OH appears to crystallize faster than C7OH and therefore exhibits a smaller crystallization exotherm. The C12OH sample crystallizes even more rapidly and therefore does not exhibit a pronounced T_g even upon rapid quenching in liquid nitrogen. The DSC scan of this rapidly quenched C12OH sample is similar to that shown in Figure 5.

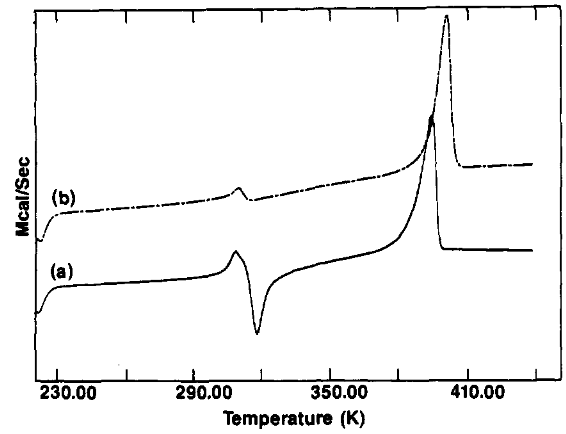


Figure 7. DSC scans of C7OH (a) and C8OH (b) after being quenched from melt into liquid nitrogen.

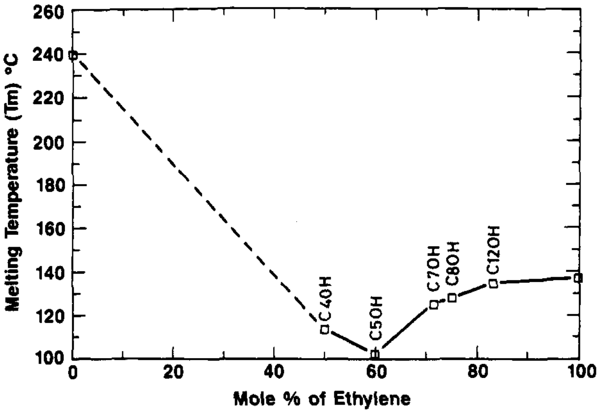


Figure 8. Melting temperature (T_m) versus composition of the C*m*OH copolymers.

The melting temperature, T_m, is plotted versus the polymer composition in Figure 8. The values of T_m used in the cases of C4OH and C5OH are those obtained from the annealed sample, and the melting points were taken as the temperature of the main melting peak. The annealed C4OH sample shows two melting transitions (Figure 6). A pronounced shoulder is observed in all the other C*m*OH polymers. This behavior has been attributed to the formation of nonequilibrium lower melting crystallites.[14] The T_m of pure poly(vinyl alcohol) (PVA) and high-density polyethylene (HDPE) represent the two extreme values in the plot. The melting points of all the C*m*OH polymers are lower than that of PVA and they do not change linearly with their composition. The T_m value drops to a minimum for C5OH (40 mol % VA) before it begins to rise and approach that of pure polyethylene. A similar behavior was observed in the case of the commercial EVAL copolymers.[15] Very little change in the melting temperatures of the commercial copolymers was observed up to 18.5 mol % vinyl alcohol, with their melting points lying in the vicinity of that of low-density polyethylene (LDPE).[15] A small drop in the melting point was observed in the composition range of 20–25 mol % VA, before it beings to rise and approach that of poly(vinyl alcohol).[16] One significant difference in behavior between the commercial EVAL copolymers and the C*m*OH polymers is the lower melting temperature of the latter samples with comparable VA content. For example, C5OH (40 % VA) and C4OH (50 % VA) have melting temperatures of 102.6

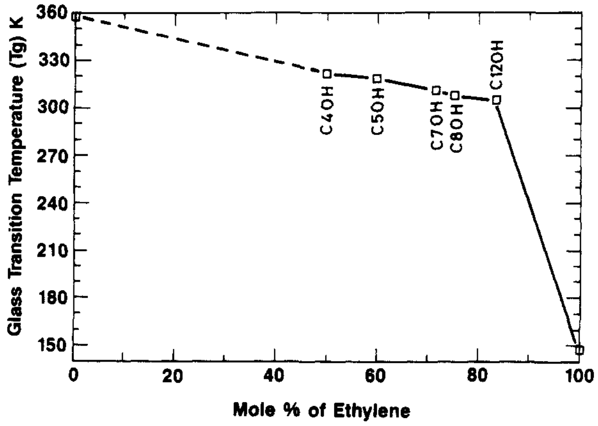


Figure 9. Glass transition temperature (T_g) versus composition of C*m*OH copolymers.

and 113.6 °C, respectively. The commercial samples having 40 and 62 mol % VA, on the other hand, melt at 141.3 and 154 °C, respectively. This significantly lower T_m of the C5OH sample compared to the commercial EVAL having the similar composition is noteworthy. Since the microstructure of the C*m*OH samples is rather well-defined, the higher T_m of the commercial samples probably reflects their heterogeneity by way of blockiness and presence of shorter diol sequences. The presence of poly(vinyl alcohol)-like segments could result in the increase of the melting temperature. The rather broad melting transition observed in the commercial samples[17] also reinforces the hypothesis regarding sample heterogeneity.

The variation of melting points with the composition in the commercial samples is in good agreement with their X-ray diffraction data, which suggested that the crystal lattices of the samples with high vinyl alcohol content (greater than 60 mol %) are isomorphous to that of pure poly(vinyl alcohol) and those with high ethylene content (greater than 80 mol % ethylene) are isomorphous to that of polyethylene. The copolymers with intermediate composition (between 20 and 60 mol % vinyl alcohol) crystallize in some intermediate pseudohexagonal crystal structure.[18] A similar behavior is likely in our copolymer samples also. While in the case of commercial EVAL copolymers the T_m approaches that of low-density polyethylene (114 °C),[15] in the case of C*m*OH the melting temperature approaches that of high-density polyethylene (137.5 °C). This is consistent with the spectral data that indicate that while the C*m*OH samples are highly regular and do not have any branching, the commercial samples have branching.

A plot of the T_g versus the composition is shown in Figure 9. Unlike the case of T_m, the T_g of the copolymers does not go through a minimum, but instead monotonically goes down with increasing ethylene content. The standard copolymer equation does not seem to be applicable in this system and the linear extrapolated value is much higher than the observed one. A similar behavior has also been observed in the commercial EVAL copolymer samples and has been attributed to the presence of hydrogen bonding in them.[19] Even at very low OH content intermolecular hydrogen bonding in the amorphous regions of the polymer appears to restrict segmental motion sufficiently to enhance the T_g significantly.

Conclusions

Complete hydroxylation of polyalkenylenes using the hydroboration–oxidation sequence represents a novel approach to the synthesis of ethylene–vinyl alcohol copolymers. Polyalkenylenes having different numbers of methylene units between the double bonds were synthesized from cycloolefins having appropriate ring sizes. The hydroboration–oxidation reaction sequence allowed the complete transformation of the double bonds along the polymer backbone into vinyl alcohol units. Thus, EVAL copolymers with vinyl alcohol content ranging from 16 to 50 mol % were synthesized. The proton and carbon-13 NMR spectra of the copolymers are remarkably simple as compared with the commercial samples due to the much smaller range of diol segments present in these copolymers, and also due to the proportional increase in spacing between the hydroxyl groups with increasing ethylene content. The melting temperatures of these copolymers decreased initially, going through a minimum at a composition of 40 mol % VA, before they began to increase again. The melting point of the copolymer with 16.7 mol % vinyl alcohol approaches that of linear high-density polyethylene.

One major limitation of this approach is the limited window of composition that is accessible. Copolymers with more than 50 mol % vinyl alcohol are difficult to prepare by this method, and those with very high ethylene content would require the use of large cycloolefins that are not readily available. However, this approach has demonstrated several advantages. It allows complete control of the composition within the permissable composition range and also control over the placement of the hydroxyl group along the polymer backbone. Further fine tuning of the composition within this range can be achieved by copolymerization of the different cycloolefins. This would, however, reduce the fine control over the spacing between the hydroxyl groups on the polymer backbone that is achievable in the case of homopolymers.

Finally, the polymers obtained by this method have no branching in them and therefore they may be considered copolymers of linear high-density polyethylene and vinyl alcohol. This is in contrast to the commercial samples, which have varying degrees of branching in them and exhibit properties that correspond to the behavior of low-density polyethylene. Therefore, these samples can serve as excellent models for understanding structure–property relationships in ethylene–vinyl alcohol copolymer systems.

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Registry No. C_4 (homopolymer), 26426-65-3; C_{12} (homopolymer), 27056-69-5; C_8 (homopolymer), 25267-51-0; C_5 (homopolymer), 25103-85-9; 1,5-cyclooctadiene (homopolymer), 26353-15-1.