378 *Macromolecules* **1990,** *23,* 378–382

Functional Group Containing Copolymers Prepared by the Ziegler–Natta Process

S. Ramakrishnan, E. Berluche, and T. C. Chung*

Corporate Research, Exxon Research and Engineering Company, Route 22 East, Clinton Township, Annandale, New Jersey 08801. *Received March 6, 1989; Revised Manuscript Received June 7, 1989*

ABSTRACT: A novel method for the preparation of functional polyolefin copolymers by the Ziegler–Natta process using organoborane monomers is presented. *B*-5-Hexenyl-9-BBN (BBN = borabicyclo[3.3.1]nonane) and 1-octene were copolymerized and further oxidized to poly(octene-*co*-hexenol). The reactivity of the borane monomer was found to be only slightly lower than that of 1-octene, thus enabling the synthesis of copolymers with a wide range of composition. The comparison of the GPC profiles from the UV and RI detectors established the homogeneity of the copolymers. The same results were also concluded from the DSC studies. A single T_g, which increased with the hydroxyl content, was observed. Although the molecular weights of the copolymers were found to be high, their GPC profiles suggested a lowering of molecular weights with increasing borane monomer in the feed. To establish the effect of a trialkylborane on the polymerization, 1-octene was polymerized with/without an equimolar amount of Et_3B, and no significant effect on the molecular weight was observed.

Introduction

The incorporation of functional groups into hydrocarbon polymers represents a useful method for modifying the chemical and physical properties of polymers, such as, permeability, compatibility, dyeability, adhesion, solid-state morphology, and solution rheology. Applications for such new materials are very broad, including plastics, elastomers, lubes, and barrier resins.

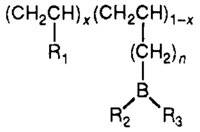
It is normally difficult to prepare homopolymers and copolymers that contain oxygen and nitrogen functionalities, by Ziegler–Natta processes. The Lewis acid components (Ti and Al) of the Ziegler–Natta catalyst tend to form a complex with the nonbonded electron pairs on nitrogen and oxygen in preference to complexation with the π electrons of the double bonds of the monomer. The net result is the deactivation of the active polymerization sites or the poisoning of the catalyst.

There are some reports of copolymerization of functional monomers with other α-olefins. For example, Clark[1] has described a method of rendering polar vinyl monomers sufficiently unreactive to allow them to copolymerize with α-olefins without destroying the Z–N catalyst. This method consists of pretreating polar monomers with an organoaluminum compound. Ester monomers are especially effective because they are less reactive with Z–N catalysts than some other oxygenated functionalities, like –COOH. Thus, copolymers of an ester, like the methyl undecylinic ester,[2] and α-olefins like ethylene, propylene, and 1-octene are reported. Nevertheless, the levels of the ester functional group incorporation for these copolymers remain low, i.e., <5 mol %. The incorporation of high levels of ester functionality requires even more sterically hindered ester monomers, such as 2,6-diphenylphenyl 10-undecanoate.[3] However, the reaction conditions for such a process are very inconvenient (e.g., 65 °C and 10 days). Moreover, the ester copolymer is not a versatile intermediate. It is difficult to convert the ester functional polymers to other functional polymers (e.g., –OH, $-NH_2$) by simple mild chemical reactions.

Organoboranes are valuable intermediates in organic synthesis.[4] However, organoborane polymers are rare, being generally limited only to polydiene, such as polybutadiene and polyisoprene,[5] backbones. Furthermore, organoborane polymers have previously been prepared only by postpolymerization modification processes, rather than direct polymerization. Generally, postpolymerization has been limited to only the few existing diene homopolymers and copolymers.

In our previous paper,[6] we described a novel method for directly preparing functional olefin homopolymers. This method involves both borane monomers and polymers that are stable to the Ziegler–Natta catalyst and serve as valuable intermediates for conversion to a host of other functional polymers, such as polyalcohol.

The present report relates to copolymers of borane monomers and α-olefin monomers, having the following formula:



R_1 is an alkyl group, R_2 and R_3 are alkyl or cycloalkyl groups, where $n > 2$ and x varies from 0 to 1. They are prepared by direct Ziegler–Natta polymerization as shown in Scheme I. The borane copolymers are useful intermediates and are readily convertible into other functional copolymers. We describe here copolymers, of 1-octene and 1-hexenyl-9-BBN, i.e., where $R_1 = C_6H_{13}$ and $n = 4$. The composition of the copolymers was varied to obtain polymers with varying hydrophobicity.

Experimental Section

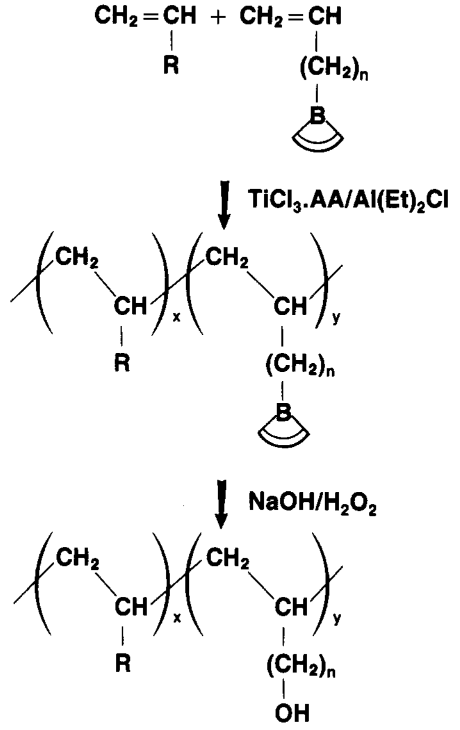
The organoboranes and Ziegler–Natta catalysts were always handled in an inert atmosphere of nitrogen or argon with careful exclusion of both oxygen and water. All glassware, syringes, and needles were oven-dried at 150 °C for 2 h before use. The hot glassware was assembled and cooled under a flow of nitrogen or evacuated in the antichamber before being moved into the drybox.

---

* Author to whom all correspondence should be addressed. Present address: Department of Material Science and Engineering, The Pennsylvania State University, University Park, PA 16802.

0024-9297/90/2223-0378$02.50/0

Scheme I



9-BBN (Aldrich), Al(Et)$_2$Cl (Aldrich), and TiCl$_3$–AA (Stauffer, pretreated with aluminum alkyl) were used as received. Analytical-grade toluene and THF were stirred with sodium naphthalide to remove any traces of water and oxygen and then distilled under nitrogen. 1-Octene and 1,5-hexadiene (Wiley) were purified by distillation from sodium metal. IR and NMR spectra were obtained with a Perkin-Elmer 298 infrared spectrophotometer and a Bruker AM 360 spectrometer, respectively. The GPC chromatograms were obtained using a Waters 600E delivery system that was connected to a Waters 410 refractometer and a 490E programmable multiwave length detector. A series of three Ultrastyragel columns with pore sizes of 10^3, 10^4, and 10^6 Å was used to effect separation. The analysis of the data was performed using a Digital professional 380 computer. The DSC thermograms were obtained using a Perkin-Elmer DSC-7 thermal analysis system. Temperature calibration was done using cyclohexane as a standard.

Preparation *B*-5-Hexenyl-9-BBN. 1,5-Hexadiene (33 g, 0.4 mol) was taken in a 250-mL round-bottom flask along with 50 mL of THF in an argon-filled drybox (Vacuum Atmospheres). 9-BBN (12.2 g; 0.1 mol) dissolved in 150 mL of THF was taken in a dropping funnel and added dropwise to a stirring solution of the diene. After the reaction was allowed to proceed for 12–16 h, the solvent was removed under vacuum, and the residual oil was subjected to fractional distillation under vacuum. The product was collected as the center cut at 60–75 °C under 6 μmHg. The product yield was 15.2 g, which corresponds to a percent yield of 74.5% based upon 9-BBN. The ^{1}H NMR spectrum was in good agreement with the expected structure of the product.

Copolymerization. Typically, the required quantity of TiCl$_3$–AA ([monomer]:[Ti] = 100) was weighed into the reaction flask, and toluene (to make a 15% monomer solution) was added to it and stirred. Et$_2$AlCl ([Al]:[Ti] = 10) was then weighed into the reaction flask. The required quantity of the two monomers was weighed and premixed in a vial, and the mixture was added to the catalyst solution. The polymerizations were allowed to proceed for about 1–2 h to attain a percent conversion of around 40–60%. The polymerization was terminated by addition of 2-propanol that caused the disappearance of the deep burgundy color of the active catalyst. The polymer was precipitated out as a white rubbery material by further addition of 2-propanol and thoroughly washed with additional 2-propanol. All the above manipulations were carried out in the drybox.

Oxidation of the Polyborane to Polyalcohol. The wet polymer sample was redissolved in THF to make a 2–3% solution. A measured quantity of 6 N NaOH solution (1.3 mol/mol of alkylborane) was degassed and added to it. The solution was cooled in an ice–water bath, and H_2O_2 (30% aqueous solution, 3.9 mol/mol of alkylborane) was added dropwise to it with stirring. The solution was allowed to warm to room temperature and then maintained at 40 °C for 12–16 h. The polymer was precipitated in water, washed thoroughly with acetone, and dried under vacuum in the presence of P_2O_5.

The poly(octene-*co*-hexenol) samples are numbered POH-13, POH-11, and POH-31, the numbers indicating the molar feed ratios of the two monomers, 1-octene and hexenyl-9-BBN, respectively. The IR spectra of the polymers were recorded using a thin film cast on a KBr plate. The ^{1}H NMR spectra were obtained using a 2–3% solution of the polymer in $CDCl_3$/CD_3OD (5:1 v/v).

Esterification. Typically, 100 mg of the polyalcohol was dissolved in 15 mL of a mixture of THF and DMF. The amount of DMF required to form a clear solution varied with the composition of the copolymers. Pyridine and benzoyl chloride were added in a 10-fold molar excess, and the reaction was allowed to proceed for 12–16 h. The polymers were precipitated in methanol, washed thoroughly, and dried under vacuum. Yields obtained varied from 105 to 125 mg.

Results and Discussion

Monomer Synthesis. The easiest way to prepare borane monomers is by selective monohydroboration of the appropriate dienes.[7] However, some previous attempts have suffered from byproducts due to both a dihydroboration reaction and nonselective hydroboration at the other double bond. For example, the hydroboration of symmetrical dienes with dialkylboranes, such as 1,5-hexadiene, with 9-borabicyclo[3.3.1]nonane (9-BBN) proceeds in an essentially statistical manner, giving 25% residual diene, 50% of the monohydroboration products, and 25% of dihydroboration products. To decrease the dihydroboration reaction, we have used a large excess of diene at low (ambient) temperature. After sufficinet time to complete the reaction, the excess diene and solvent was recovered by reducing the pressure, followed by distillation of the pure borane monomers at a higher temperature. In this manner, a series of borane monomers, such as *B*-4-pentenyl-9-BBN, *B*-5-hexenyl-9-BBN, and *B*-7-octenyl-9-BBN, has been synthesized. On the basis of preliminary observations, 1-octene and *B*-5-hexenyl-9-BBN appeared to have comparable reactivity. Therefore, a detailed investigation of this copolymerization was undertaken.

Copolymerization. The copolymerization of borane monomers with other hydrocarbon monomers and the further conversion of the borane moiety into a hydrophilic functionality is a viable approach to fine tune the hydrophilicity of hydrocarbon polymers. Large differences in reactivities of the monomers often result in variation of composition during polymerization. To study the difference in reactivities between the two monomers, the copolymerization of 1-octene and *B*-5-hexenyl-9-BBN was studied as a function of conversion. The composition of the copolymers was determined by ^{1}H NMR and will be discussed in the following section. Figure 1 is a plot of percent incorporation of 1-hexanol as a function of conversion. The plot shows a small increase in the 1-hexanol content (from the *B*-5-hexenyl-9-BBN monomer) in the copolymer with increasing conversion, suggesting a slightly higher reactivity of 1-octene as compared to *B*-5-hexenyl-9-BBN. The order of addition of the cocatalyst, Et$_2$AlCl, and monomer causes a small difference in the composition of the resulting copolymers. The activation of the catalyst prior to addition of the

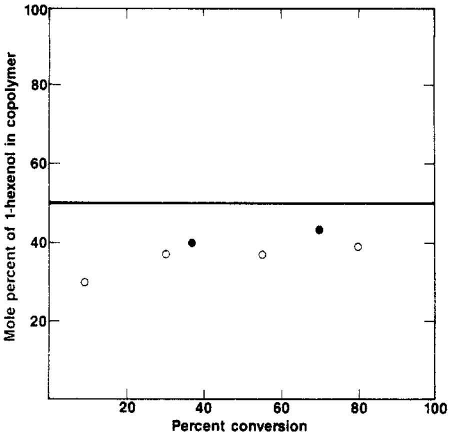


Figure 1. Plot of composition of the copolymers versus percent conversion. Et_2AlCl addition (○) prior and (●) after addition of the monomer.

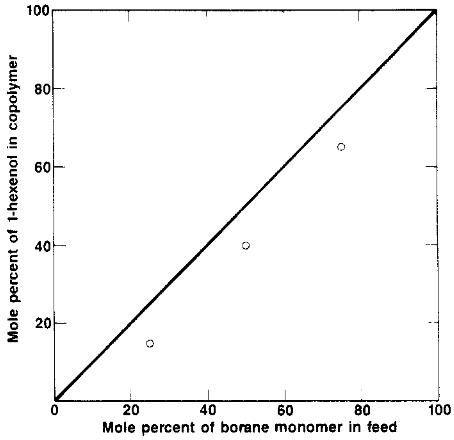


Figure 2. Plot of copolymer composition versus feed composition.

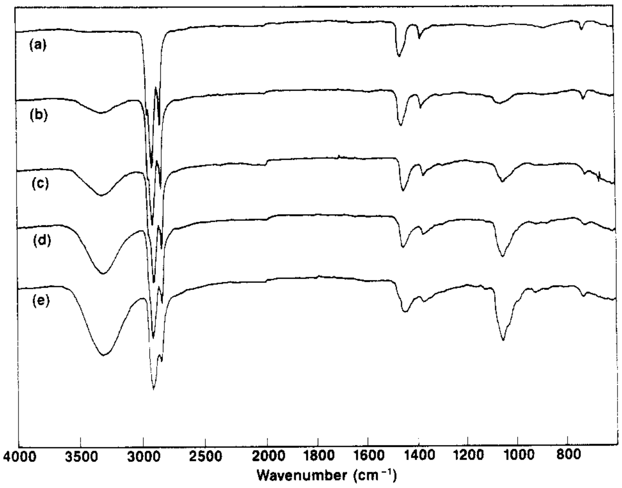


Figure 3. IR spectra of the homopolymers and copolymers: (a) poly(1-octene), (b) POH-31, (c) POH-11, (d) POH-13, (e) poly(1-hexenol).

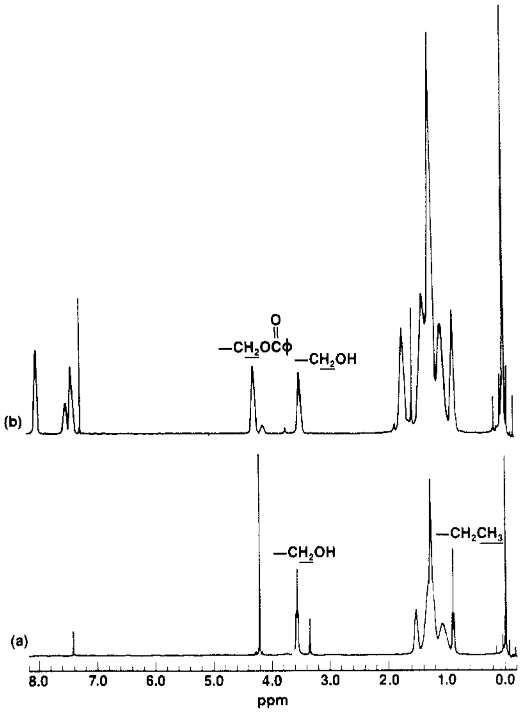


Figure 4. ^1H NMR spectra of the copolymer POH-13 (a) before and (b) after esterification.

monomers results in a slightly higher incorporation of 5-*B*-hexenyl-9-BBN. In general, the drift in composition with percent conversion was found to be small and hence, the copolymerizations with varying monomer feed ratios were allowed to proceed to about 40–60% conversion. The homogeneity of the copolymer composition under these conditions was considered reasonable, as will be proved later. The feed vs composition plot (Figure 2) indicates that the percent incorporation of the borane monomer is consistently lower. This suggests a slightly lower reactivity of the borane monomer as compared to 1-octene. No attempts were made to determine their reactivity ratios, as the percent conversion of ~50% is considered too high for such calculations.

Structure and Composition of Copolymers. (a) IR and NMR Studies. Due to the very high susceptibility of alkylboranes to air oxidation, the borane polymers were not structurally characterized. The borane polymers were instead quantitatively oxidized under mild conditions, using alkaline H_2O_2, to yield polyalcohols. The copolymers were insoluble in most common organic solvents. However, they were completely soluble in mixed solvents, such as THF–methanol and chloroform–methanol. The relative amounts of alcohol required increased with the amount of 1-hexenol in the copolymers, with polyhexenol being completely soluble in pure methanol and polyoctene being completely soluble in THF. The polyalcohols were characterized by IR and NMR spectroscopy. The IR spectra (Figure 3) of the copolymers indicate a steady increase in the hexenol content with increasing borane monomer in the feed, as indicated by the increase in the intensity of the –OH stretching absorption.

A typical ^1H NMR spectrum of the copolymer is shown in Figure 4a. The composition of the copolymers was calculated using the intensities of the methylene protons α to the hydroxyl group (δ = 3.6) and the terminal methyl protons (δ = 0.9) of 1-octene. These values are listed in Table I. A mixed-solvent system of $CDCl_3$–CD_3OD was used to obtain the NMR spectra, as the polymers were insoluble in a single solvent.

(b) GPC Studies. As mentioned earlier, the extreme difference in solubility of poly(1-hexenol) and polyoctene resulted in the copolymers being insoluble in common solvents that are suitable for GPC. Hence, the copolymers were esterified with benzoyl chloride. The IR spectra of the esterified copolymers indicated an almost complete disappearance of the –OH stretching absorption. However, their ^1H NMR spectra indicated that the

Table I[a]

sample	mol % 1-octene		GPC data[b]				
	in feed	in copolymer[c]	$M_n \times 10^{-3}$	peak M × 10^{-3}	M_w/M_n	T_g,[c] °C	(onset)
poly(1-octene)	100	100	329	1670	5.1	−67	(−75)
POH-31	75	85	242	1580	6.1	−51	(−66)
POH-11	50	60	126	1030	7.8	−26	(−50)
POH-13	25	35	66	280	6.0	2	(−16)
poly(1-hexenol)	0	0	55	120	2.6	15	(7)

[a] Determined by ^{1}H NMR. [b] GPC was done on partially benzylated polyalcohols. [c] T_g taken as the inflection point and the number in parentheses in T_g taken on the onset.

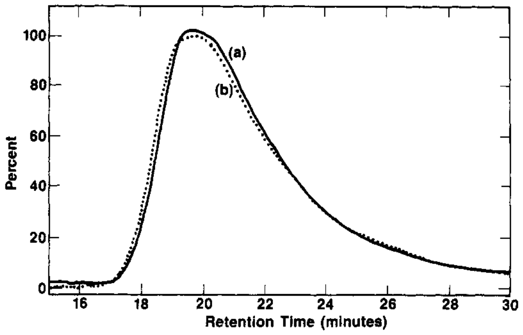


Figure 5. Typical GPC profiles of esterified copolymer POH-11 (a) using RI detector and (b) using UV detector.

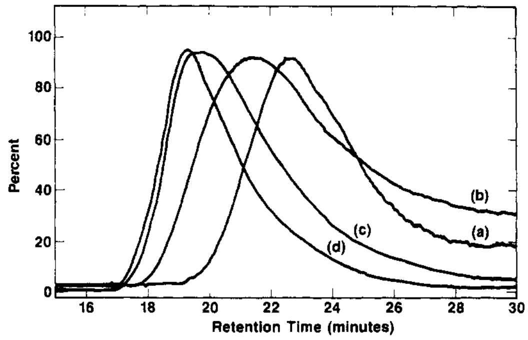


Figure 6. GPC profiles of various esterified copolymers: (a) poly(1-hexenol), (b) POH-13, (c) POH-11, (d) POH-31.

esterification was only partially complete. A typical spectrum of a partially esterified copolymer is shown in Figure 4b. Calculations based upon the integrated intensity of the methylene hydrogens α to -OH and α to -OCO ϕ (which appears at δ = 3.5 and δ = 4.3, respectively) indicated an average percent esterification of only about 50–55%. The partially esterified polymers were, however, completely soluble in THF and, therefore, were used for molecular weight determination by GPC. The use of phenyl ester permits the use of both UV and refractive index detectors. The UV detector was set at an observation wavelength of 254 nm. Since the chromophore, i.e., the phenyl ester group, is present only in one of the monomers, the comparison of the two chromatogram profiles (Figure 5) serves as an indication of the homogeneity of the copolymer samples, considering of course a statistical distribution of the ester functionality in the polymer chains (bearing in mind that only about 50% esterification has taken place). The small shift in one of the curves, with respect to the other, arises because the eluted fractions pass through the UV detector 0.25 min before passing through the RI detector due to the instrument configuration. The almost exact overlap of the UV and RI profiles is a strong indication of the homogeneity of the copolymer samples.

The GPC chromatograms (Figure 6) of the various copolymers indicate an increase in the peak retention times with increase in the mole percent borane monomer in the feed. If this reflects a lowering of molecular weights, it appeared that chain transfer to the trialkylborane may be a likely explanation.[8] In order to completely understand the effect of trialkylborane on the molecular weight of the polymer by the Z–N process, homopolymerization of 1-octene was carried out in the presence an equimolar amount of Et_3B. The overall set of conditions used was $TiCl_3$/10 Et_2AlCl/100 Et_3B/100 octene. The GPC curves from such an experiment are shown in Figure 7. Initially it appeared that the trialkylborane caused the increased tailing (peak retention time being the same, curve a). A further experiment under the same conditions but at lower conversion (curve c), however, indicated that the tailing was an inherent property of the Z–N process, rather than the effect of borane. This experiment conclusively proved the absence of any retarding effect in the molecular weight due to the presence of alkylborane monomer. The higher retention time, therefore, is probably an effect of the presence of increasing amounts of functional groups (-OH and $-OCOCH_3$) rather than an actual decrease in molecular weight. The changes in the hydrodynamic volume and/or some kind of interaction of the functional groups with the column could cause such a behavior. Further experiments, such as light scattering could give a better understanding of this behavior.

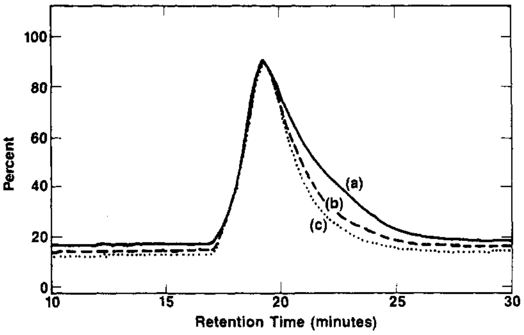


Figure 7. Effect of Et_3B and percent conversion on the GPC profiles of poly(1-octene). Curves (a) and (c) represent profiles using a catalyst combination, $TiCl_3$/10 Et_2AlCl/100 Et_3B/100 1-octene, at 83% and 23% conversions, respectively, and (b) represents a 56% conversion in the absence of Et_3B.

Thermal Properties. Thermal analysis of the polymers was done using DSC. The samples were first heated to 175 °C in the DSC pans and retained at that temperature until there was no further heat uptake (~5–10 min). They were then rapidly cooled (~100 deg/min) to −140 °C. The curves shown in Figure 8 are heating curves obtained from these quenched samples at a heating rate of 20 deg/min.

All the copolymers exhibited a single glass transition temperature (T_g), which lies between those of the two homopolymers. The presence of only one glass transition is taken as evidence for the absence of macroscopic phase separation and therefore implies that the copolymer samples are fairly homogeneous. This is also often

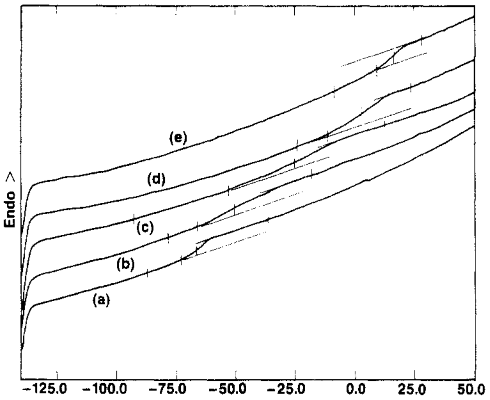


Figure 8. DSC curves of the homopolymers and copolymers using a heating rate of 20 deg/min: (a) poly(1-octene), (b) POH-31, (c) POH-11, (d) POH-13, (e) poly(1-hexenol).

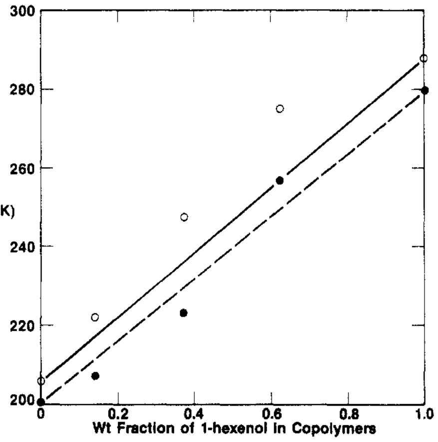


Figure 9. Plot of composition of the copolymers versus their glass transition temperatures. (○) T_g taken as the inflection point and (●) T_g taken as the intersection of the base line and the extrapolation of the inflection.

taken as an indication of randomness as opposed to blockiness of the copolymers. The glass transition temperatures may either be taken as the inflection point, i.e., the center of the transition or as the onset of the transition.[9] Both these values are given in Table I. The difference between these two values, ΔT_g, is an indication of the width of the transition. As one would expect, any random copolymer is inherently less homogeneous than the homopolymers and, therefore, the ΔT_g is larger in the former case.

A plot of composition of the copolymers versus T_g is shown in Figure 9. A monotonic drift in the T_g of the copolymers away from the linear relationship is observed when the inflection point is taken as T_g. On the other hand, the glass transition temperatures are randomly distributed along the line when they are taken as the onset temperatures. A linear relationship between the glass transition temperature and the weight fraction of either monomer has been taken as an indication of the homogeneity of the copolymer samples.[10] The DSC profiles of the copolymers and the variation of T_g with composition give a qualitative indication of the homogeneity and random nature of the copolymer samples.

Conclusion

The preparation of functional polymers by direct Ziegler–Natta polymerization has long been a goal of synthetic polymer chemists. Progress has been impeded because of the dearth of functional groups that are stable to Ziegler–Natta catalysts. A new method for the synthesis of copolymers of α-olefins and functional monomers has been developed based on borane monomers and polymers. Copolymers of 1-octene and 1-hexenol were synthesized using this approach, and the homogeneity of the copolymer samples was established. The 1-hexenol content in the copolymers was varied to get copolymers of varying hydrophilicity. The value of this method rests with the "cleanliness" and versatility of its chemistry. Not only can the borane derivatives be quantitatively carried through the Ziegler–Natta process, but they can also be quantitatively converted to a host of other functionalities.

Acknowledgment. The discussions with H. C. Brown were very helpful in understanding boron chemistry.

Registry No. (1-Octene)(1-hexenyl-9-BBN) (copolymer), 117381-36-9; *B*-5-hexenyl-9-BBN, 112741-05-6; 9-BBN, 280-64-8; $TiCl_3$, 7705-07-9; Et_2AlCl, 96-10-6; Et_3B, 97-94-9; 1,5-hexadiene, 592-42-7.

References and Notes

(1) Clark, K. J.; City, W. G. U.S. Patent 3,949,277, 1970.
(2) Schulz, D. N.; Kitano, K.; Burkhardt, T. J.; Langer, A. W. U.S. Patent 4,518,757, 1984.
(3) Purgett, M. D. Ph.D. Thesis, University of Massachusetts, 1984.
(4) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1973.
(5) Pinazzi, C.; Broose, J. C.; Pleudeam, A.; Reyo, D. *Appl. Polym. Symp.* **1975**, *26*, 73.
(6) Chung, T. C. *Macromolecules* **1988**, *21*, 865.
(7) Liotta, R.; Brown, H. C. *J. Org. Chem.* **1981**, *42*, 2836.
(8) Chain transfer to organoaluminum has been hypothesized for a conventional Z–N process. Keii, T. *Kinetics of Ziegler–Natta Polymerization*; Chapman and Hall; London, 1973.
(9) Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley-Interscience: New York, 1980; p 565.
(10) Deviations from linearity often result from differences in thermal expansion behavior. The equation commonly used, is $T_g = (KW_1T_{g\,1} + W_2T_{g\,2})/(KW_1 + W_2)$ were W_1, W_2, $T_{g\,1}$, and $T_{g\,2}$ are weight fractions and glass transitions of the two homopolymers, respectively. $K = \Delta\alpha_2/\Delta\alpha_1$ where $\Delta\alpha_1 + \Delta\alpha_2$ are the differences in thermal expansion coefficients of respective homopolymers, before and after glass transition. Deviations from linearity are often seen when $K \neq 1$.[9]