Novel Polymeric Alcohols by Controlled Catalytic Polymer Functionalization

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SYNOPSIS

Novel EPDM (ethylenepropylenediene monomer) and polybutadiene polyols can be synthesized by a two-step process of controlled hydroformylation and then reduction of the formyl groups to place a desired amount of pendant alcohol groups along the polymer chain. The degree of functionalization can be controlled by measuring gas uptake from a calibrated reservoir during hydroformylation. Hydroformylation can be performed in solution or under simulated melt-phase conditions using either $HRh(CO)(PPh_3)_3$ or $Rh(acac)(CO)_2$ as catalysts. Reduction of the polyaldehyde by $NaBH_4$ generates the polymeric alcohol without further reaction of the remaining double bonds. Polymer functionalization and further modifications were followed by ^1H-NMR and FTIR. These unique hydrophobic polyols can be reacted further to produce other polymer systems. As an example, urethanes have been made with these polyols by reaction with diisocyanates. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In this article, we describe materials prepared by selective functionalization of olefin-containing polymers to produce novel EPDM and polybutadiene polyols with the pendant —OH groups distributed along the polymer backbone. With the methods that we employ, we can readily control the amount of hydroxy functionality on either EPDM or polybutadiene polymers at a variety of molecular weights. We also discuss various physical properties of polyurethanes made from these materials.

In the experimental sections of this article, we also describe our refinements to the methods of reacting a specific number of double bonds on a diene polymer to "dial in" a specific amount of functionality without an unwanted side reaction that can cause crosslinking or an unnecessary reaction of the remaining double bonds. Varying the polymer functional density allows the effect of polyol functionality on urethane properties to be investigated with-

out changing the molecular weight of the polyol as well.

Polymeric alcohols, polyols, can be reacted with polyfunctional isocyanates to form polyurethane materials. By varying the structure and properties of the polyol segment, the physical properties of the polyurethane can be altered to make materials with a wide variety of uses such as flexible and rigid foams, elastomers, thermoplastics, and coatings.[1] Many conventional polyurethane systems[1] use polyether- or polyester-based polyols. Polyether and polyester polyols, however, are subject to eventual oxidative, hydrolytic, and thermal degradation at the carbon–oxygen bonds of the polyol backbone,[2] and for this reason, there is continued interest in the urethane industry in hydrophobic, carbon–carbon backbone polyols. Polyurethanes have been made from hydroxy-terminated hydrocarbon polyols, such as hydroxy-terminated polybutadiene[3-5] and telechelic polybutylene,[6] which contain from two to three hydroxyl groups per chain. Such materials have been shown to have superior thermal and hydrolytic stability in comparison to polyether-based polyurethanes.[3]

Metal-mediated reactions on polymers offer another way of preparing hydrophobic polyols. Stoi-

Table I   Comparison of Methods Used to Determine Functional Density of Polyols

Gas Uptake	^{1}H-NMR	ASTM-OH Number
3.5 — OH/chain	3.4 — OH/chain	3.3 — OH/chain
5 — OH/chain	4.8 — OH/chain	5.0 — OH/chain
7 — OH/chain	6.95 — OH/chain	6.92 — OH/chain

chiometric methods for functionalizing polybuta-diene using hydroboration have been reported[7]; however, these methods require very rigorous air- and moisture-free conditions. Hydroxymethylation of polybutadiene by various techniques has been described previously in the literature.[5,8–14] Some early work using homogeneous cobalt catalysts[11] suffered from a lack of selectivity and crosslinking of the final product. Hydroformylation of double-bond-containing polymers using rhodium complexes was reported by Sanui et al.[12] and Azuma et al.[10] Up to 20% of the original double bonds on a polymer, such as a polypentenamer[12] or polybutadiene,[10] could be functionalized with formyl side groups; however, a considerable amount of crosslinking was encoun-tered upon reduction of hydroformylated polybu-tadienes with sodium borohydride-based reagents to make polyols.[10] Mohammadi et al.[8] also reported the hydroformylation of polybutadienes using homo-geneous rhodium catalysts to provide polymers with up to 20% of the available double bonds hydrofor-mylated. The hydroformylated polybutadiene was then reduced using a homogeneous ruthenium cat-alyst which reduced the formyl groups to hydroxy-methyl groups and saturated the remaining double bonds.[8] However, to our knowledge, the literature does not report a general, convenient methodology for selectively, introducing controlled amounts of nonterminal hydroxy functionality onto olefin-con-taining, hydrocarbon backbone polymers. Recently, Tremont et al.[13] reported the hydroformylation of polybutadienes using HRh(CO)(PPh₃)₃ and excess PPh₃ (ratio 1 : 165) to produce stable hydroformyl-ated polymers with up to 80% of the available double bonds functionalized with formyl groups. The con-

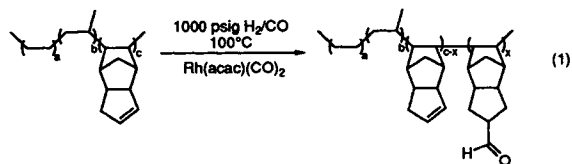version of these materials to polyols is discussed in this report.
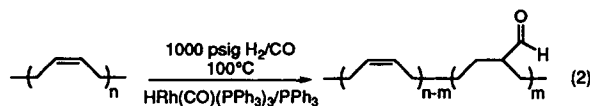
RESULTS AND DISCUSSION

The ability to functionalize a specific average num-ber of double bonds in an olefin-containing polymer to produce a soluble, functionalized polymer with a known amount of double bonds left for further reac-tivity could be the basis for producing a wide variety of complex macromolecular structures that would be very difficult to produce using traditional poly-merization techniques. We used careful gas-uptake techniques during hydroformylation and an appro-priate choice of catalyst systems to introduce specific amounts of functionality to the polymer backbone while minimizing side reactions which can lead to crosslinking or an unwanted reaction of more of the double bonds in the polymer. It is this ability to "dial in" the functional density that we have taken advantage of to produce our hydrocarbon polyols.

Solution Hydroformylation

Hydroformylation of EPDM (ethylenepropylene-diene monomer) polymers was performed in solution and in the solid state. The extent of functionaliza-tion set by monitoring gas uptake could be confirmed by FTIR and comparison of the integrals for the aldehyde protons and the olefin protons in the ^{1}H-NMR. While the FTIR was usually used to identify that aldehyde groups were present in the polymer, ^{1}H-NMR was used to further confirm the level of functionality. Percent conversions determined by ^{1}H-NMR coincided well with gas-uptake data listed in Table I.

It was found that for EPDM polymers Rh(acac)(CO)₂ (acac = acetylacetonate) was as ef-fective a catalyst for hydroformylation as was HRh(CO(PPh₃)₃/PPh₃. Rh(acac)(CO)₂ could be used to hydroformylate EPDM polymers with as lit-tle as 10 ppm catalyst concentration vs. polymer present in the reaction mixture [Eq. (1)]. A clean-

Scheme 1

$$\text{-(CH_2-CH=CH-CH_2)-}_n \xrightarrow[\text{HRh(CO)(PPh}_3)_3/\text{PPh}_3]{\substack{\text{1000 psig H}_2/\text{CO} \\ 100^\circ\text{C}}} \text{-(CH_2-CH=CH-CH_2)-}_{n-m}\text{-(CH_2-CH-CH_2-CHO)-}_m \quad (2)$$

Scheme 2

up step is often not necessary to remove such small quantities of catalyst from the reaction mixture. The polymer can often be taken on to the next reaction without any interference from the residual catalyst.

In the case of polybutadienes, $Rh(acac)(CO)_2$ worked well for low-conversion reactions (less than 10% of the double bonds to be functionalized) but catalyst deactivation hindered attempts to go to higher conversions. $HRh(CO)(PPh_3)_3/PPh_3$ was found to be a much better catalyst system for hydroformylating polybutadienes to high conversions without crosslinking [Eq. (2)].[13] $HRh(CO)(PPh_3)_3$ without added PPh_3 showed much slower deactivation than did $Rh(acac)(CO)_2$ and was used for polybutadiene hydroformylation in the present work.

Simulated Melt-Phase Hydroformylation

Hydroformylation of EPDM polymers was also demonstrated in a simulation of melt-phase condi-

tions. Solventless, simulated melt-phase hydroformylation was accomplished by first dissolving an EPDM and a Rh catalyst [$HRh(CO)(PPh_3)_3$ or $Rh(acac)(CO)_2$] in toluene to completely disperse the catalyst in the polymer and then removing the toluene under vacuum. The thick film of EPDM (0.1–1.0 g) was then placed in a stainless-steel reactor and heated above its melting point to 150°C. The reactor was charged with 1000 psig of H_2/CO. Due to the small scale in this preliminary melt-phase study, quantification of aldehyde by gas uptake was not obtained. ^{1}H-NMR and FTIR (see Table II) revealed that both $Rh(acac)(CO)_2$ and $HRh(CO(PPh_3)_3$ were capable of hydroformylating EPDM polymers under these conditions at the 10 pph catalyst to polymer level. Trace amounts of aldehyde could be observed in the ^{1}H-NMR when the reaction was run with as low as a 10 pph catalyst to polymer level. Trace amounts of aldehyde could be observed in the ^{1}H-NMR when the reaction was run with as low as a 10 ppm catalyst to polymer ratio.
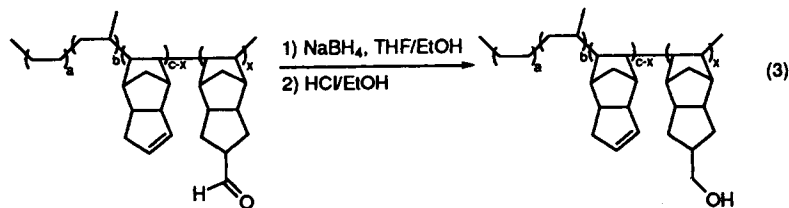
Reduction to Polyols

Reduction of hydroformylated polymers by hydrogenation with transition-metal catalysts has been reported previously[8,14]; however, the catalytic con-

Table II Simulated Melt-phase Hydroformylation

EPDM (g)	Catalyst	Catalyst (g)	Concn[a]	Temp (°C)	CO/H$_2$ (psig)	Time (min)	FTIR	^{1}H-NMR
1.0	None	0.0	0	150	1000	4275	IR shows no aldehyde	^{1}H-NMR showed no aldehyde. Olefin had isomerized
1.00	A	0.01	1 pph	150	1000	1110	IR shows aldehyde at 1730 cm^{-1}	^{1}H-NMR shows no olefin and three aldehyde peaks between 9.45 and 9.75 ppm
1.00	A	0.001	0.1 pph	150	1000	1050	IR shows aldehyde peak at 1732 cm^{-1}	^{1}H-NMR shows approximately 50% olefin at 5.1 ppm and 5.4 ppm (isomerized). Two aldehyde peaks at 9.55 and 9.75 ppm
1.00	A	0.0001	100 ppm	175	1000	1140	IR shows aldehyde peak at 1732 cm^{-1}	^{1}H-NMR shows olefin and trace aldehyde
1.00	A	0.00001	10 ppm	200	1000	1080	IR shows trace aldehyde peak at 1732 cm^{-1}	^{1}H-NMR showed trace aldehyde
1.00	A	0.0001	1 ppm	200	1000	4115		^{1}H-NMR showed no aldehyde. Olefin had isomerized

Catalyst A: Hydrido carbonyl tris(triphenyl phosphine) rhodium (I).
[a] Concentration of catalyst to polymer.

Scheme 3

ditions under which aldehyde groups were reduced to hydroxy methyl groups also reduced the unreacted double bonds in the polymer backbone. We were interested in a more selective route to polyols which reduce only aldehyde groups and leave the unreacted double bonds for potential further functionalization. Stoichiometric reduction of polyaldehydes using $NaBH_4$ has been reported[10]; however, significant crosslinking in the final product was seen with polybutadiene-based polyaldehydes.[10] In our hands, $NaBH_4$, in the presence of an adequate proton source, was effective at reducing both EPDM and polybutadiene polyaldehydes to polyols without significant crosslinking [Eqs. (3) and (4)]. Reduction was performed by dissolving the polyaldehyde in THF and then adding a significant amount of ethanol to the solution before addition of the $NaBH_4$ (500 mL THF/70 mL EtOH). We found that the proton source helped to complete the borohydride reduction and prevented hydroxy groups on the polymer from complexing with the borate anions to form an extended crosslinked ionomer. Crosslinking was further prevented by quenching the reduction with $1M$ HCl in ethanol. The acid served a dual purpose of quenching any remaining $NaBH_4$ and preventing the newly formed hydroxymethyl groups from complexing to the borate anions in solution.

At this point, ^{1}H-NMR confirmed the conversion of aldehyde groups to hydroxymethyl groups and —OH functional density can be confirmed by standard ASTM hydroxide group analysis (ASTM E222).[15] We can see that by comparing our original gas-uptake data with ^{1}H-NMR of the polyaldehydes and comparing those to the ASTM —OH numbers for the polyols in Table I that our functional density can be fixed by hydroformylation and then carried through to the production of polyols.

Both EPDM and polybutadiene polyols were found to have greater thermal stability than that of poly(tetramethylene oxide) (PTMO-2000, MN = 2000, functionality = 2.0). Thermogravametric analysis (TGA) showed that the EPDM and polybutadiene polyols were stable to approximately 350°C before thermal degradation occurred, whereas PTMO-2000 was only stable to approximately 250°C (Fig. 1). The thermal stability of our polyols, made by controlled transition-metal functionalization, is similar to other hydrocarbon-based polyols such as hydroxy-terminated polybutadiene, R-45HT (M.N. = 2768.97, functionality = 2.3). Figure 2 shows the TGA curves for several of our EPDM-based polyols made from the same starting EPDM with varying degrees of hydroxyl groups per chain. The number of hydroxymethyl groups per chain does not appear to significantly affect the thermal stability of the EPDM polyols tested.

The viscosity of EPDM and polybutadiene polyols increases with increasing numbers of hydroxyl groups on the polymer. Figure 3 shows the log of viscosity as a function of temperature for a series of polybutadiene polyols made from the same starting material but with differing amounts of hydroxymethyl groups attached to the backbone. The increase in viscosity in presumably due to an increase in hydrogen bonding of the hydroxymethyl groups.

Reaction with Diisocyanates

Both the EPDM and polybutadiene polyols made for this study readily reacted to form polyurethanes. It was also noted that the primary alcohol groups on an EPDM polyol made for this study reacted with isocyanates faster than 2000 MW polypropylene glycol, PPG-2010, and hydroxy-terminated polybutadiene polyol R-45HT (Fig. 4).
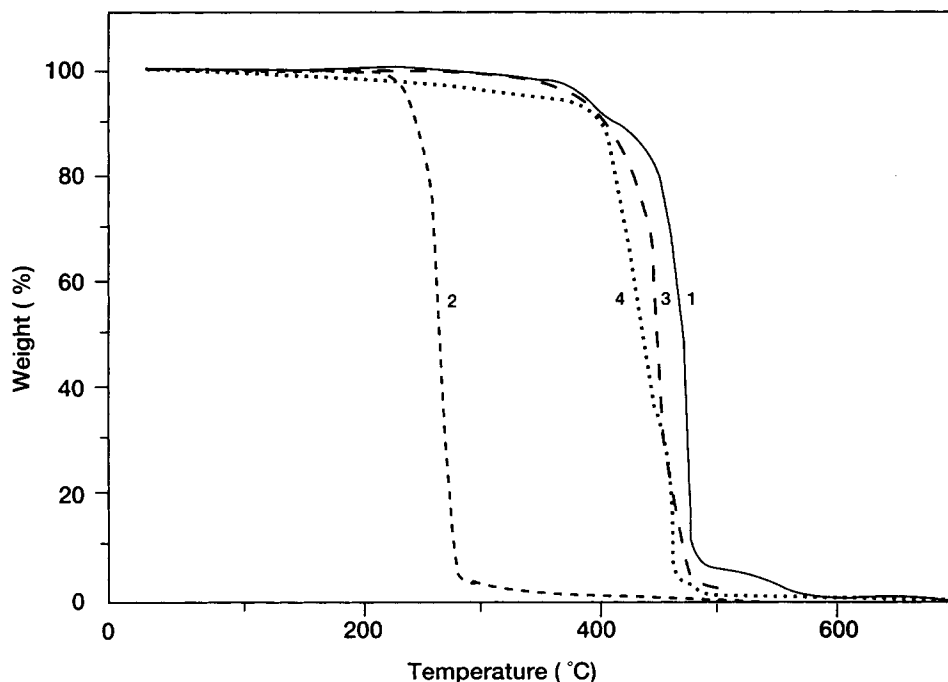
The polyurethane films made from EPDM and
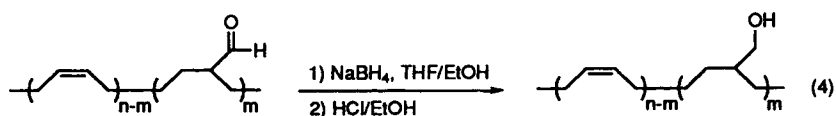
Scheme 4

Figure 1   Thermogravametric analysis—comparison of EPDM-based polyols to poly-
butadiene and PTMO-2000: 1 (——) commercial polybutadiene polyol R-45HT; 2 (---)
PTMO-2000; 3 (— — —) EPDM 3.7 OH/chain; 4 (· · ·) EPDM 3.0 OH/chain.

polybutadiene polyols exhibit a higher thermal sta-
bility than do urethanes made from polyether-based
polyols. This can been seen as a direct result of the
higher thermal stability of the polyol portion of the
urethane (Fig. 5).

EPDM 3.0, 3.9, and 5.0 in Table III were made
from the same 5000 MN EPDM starting material
and functionalized with increasing levels of hy-
droxymethyl groups. By comparing urethanes made
with similar formulations (the same amount of 1,4-
butanediol chain extender) from EPDM polyols 3.0,
3.9, and 5.0, we can compare the effect of increasing
functional density on the physical properties of the
urethane. As we can see from Table III, by increasing
the functional density of the EPDM polyol, we can
greatly increase the ultimate strength of the poly-
urethane and also increase the elongation at break.
This is also seen by comparing polybutadiene polyols
P(bd) 2.6 and 7.6 from Table III. P(bd) 2.6 and 7.6
were made from the same 4500 MN polybutadiene
with 45% 1,2-butadiene units.

The properties of the final urethane can also be
modified by addition of other agents, such as chain
extenders like 1,4-butanediol, to the formulation.
The effect of 1,4-butanediol on the ultimate
strength and elongation at break of the urethanes
made from the functionalized EPDM and poly-
butadiene polyols follows the same trends de-
scribed in the literature for urethanes made from
hydroxy-terminated polybutadienes.[3,4] Increasing
the ratio of 1,4-butanediol to polyol greatly in-
creases the ultimate strength of the urethane.
While, overall, elongation at break tends to de-
crease from the lowest amounts of chain extender
to the highest amount of chain extender, EPDM
3.9 showed its highest elongation at break at a
1 : 1 ratio of 1,4-butanediol to polyol and P(bd)
2.6 and P(bd) 7.6 showed their highest elongations
at break at a 1 : 2 ratio of 1,4-butanediol to polyol.
Previous studies of urethanes made from hydroxy-
terminated polybutadiene have also shown an op-
timum ratio of chain extender to polyol for the
highest elongation at break. The exact properties
of the final urethane can be tailored by changing
the functional density on the polyol and balancing
this effect with the amount of other agents in the
formulation, such as the amount of chain extender
added. By comparing the urethane made with
P(bd) 2.6 and a 1 : 1 ratio of 1,4-butanediol to the
urethane made from P(bd) 7.6 with a 1 : 0 ratio of
1,4-butanediol, two urethanes of similar ultimate
strength were produced (619 vs. 662); however, the
two urethanes have different elongations at break
(90% vs. 226%). Synthesis of polyols by the con-
trolled functionalization of olefin-containing
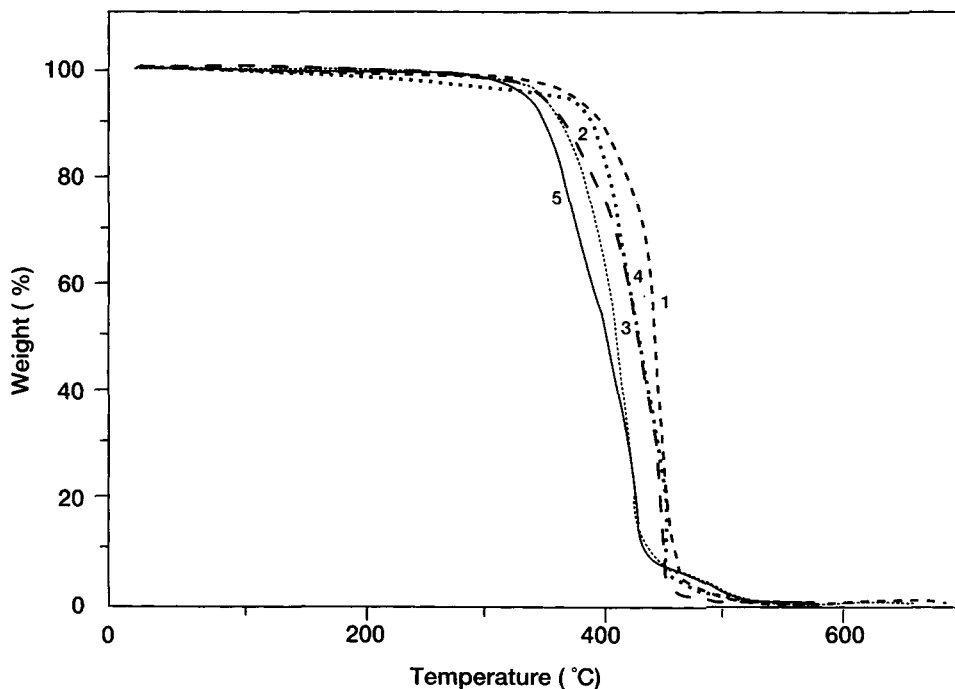polymers can provide another tool for fine-tuning

Figure 2   Thermogravametric analysis—EPDM-based polyols of differing functionality:
1 (– – –) EPDM 3.7 OH/chain; 2 (— — —) EPDM 2.5 OH/chain; 3 (- - - -) EPDM 5.0 OH/
chain; 4 (· · ·) EPDM 3.0 OH/chain; 5 (——) EPDM 4.0 OH/chain.

the macroscopic properties of urethane materials in cases where the use of a hydrophobic, hydrocarbon-based polyol would be appropriate.

EXPERIMENTAL

EPDM polymers used were Trilene 55® obtained from Uniroyal Chemical and Nordel 1440 obtained from DuPont Co. Polybutadiene was obtained from Aldrich Chemicals (Catalog No.: 20,050-6; MW_n 4500, 45% vinyl, 55% cis- and trans-1,4). Rh(acac)(CO)$_2$ (acac = acetylacetonate) and HRh(CO)(PPh$_3$)$_3$ were obtained from Strem Chemicals and used as received. 1,4-Butanediol was obtained from GAF Corp. and was dried over 4 Å molecular seives. The 4,4'-methylene bis(cyclohexylisocyanate) was obtained from Mobay Chemical Co. (sold as Desmodur W) and was used as received. The isocyanate number for urethanes was determined by the di-n-butylamine method (ASTM D-1638-74). The OH number for the polyols was determined using ASTM E-222. The stress–strain properties were measured according to ASTM D-410 (utilizing a Universal Instron Tester) and the hardness (Shore A) was measured according to ASTM D-2240.

Production of Polyaldehydes

EPDM and polybutadiene polyaldehydes were produced in a 2 L, high-pressure, calibrated gas uptake autoclave system similar in design and operation to that described previously by Tremont et al.,[13] with the exception that for the present work the autoclave was modified to include a remote operation catalyst charging device. In this system, the extent of reaction is followed by tracking the temperature and pressure of a calibrated reservoir containing a high-pressure supply of the reagent gas as it is drawn into the reactor across a gas regulator, which sets the reaction pressure.

The catalyst-charging device, shown schematically in Figure 6, features two charge pots in series, both of which are pressure equilibrated with the reactor headspace via tubing (A and B in Fig. 6). These charge pots were N$_2$ purged immediately prior to the run and filled under a nitrogen stream by direct transfer from bottles of a degassed solution. The lower pot was charged with a solution of the hydroformylation catalyst. The upper pot was charged with degassed solvent and was used as a chaser to rinse residual catalyst from the lower pot into the reactor shortly after initial catalyst addition. Both additions were controlled by remotely actuated pneumatic valves.
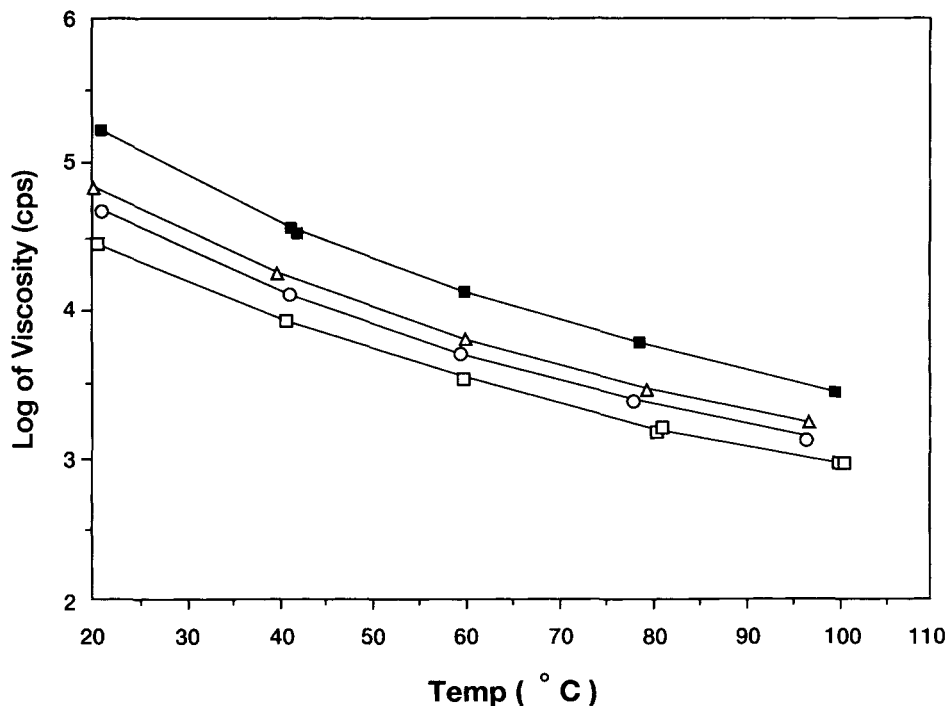
NOVEL POLYMERIC ALCOHOLS

Figure 3 Polybutadiene polyol viscosity. Polybutadiene polyols functionalized with (□) 2.9 OH/chain; (○) 3.3 OH/chain; (△) 3.4 OH/chain; (■) 4.6 OH/chain.

The primary benefit of this device is that the catalyst can be held out of the reaction mass until the reactor is brought to full pressure and temperature equilibrium at the desired set points. At "time zero," the catalyst could then be drained and rinsed into the reactor, which, by virtue of the pressure-equilibrating lines between the reactor head space and the charge pots, suffers no pressure upset or other transients. This affords a completely unambiguous set of time, pressure, and temperature initial conditions for the reaction. This enhances the precision of the gas-uptake calculations and is especially useful for fast catalyst systems and/or low target conversions.

Production of EPDM Polyaldehyde

A solution of EPDM polymer (300.05 g) in 500 mL of toluene sparged with argon was placed in the 2 L reactor and degassed three times with nitrogen. $Rh(acac)(CO)_2$ (75.3 mg, 0.292 mmol) in 100 mL of toluene under argon was placed in the catalyst addition charge pots. The reactor was heated to 100°C and charged with 1000 psig with 1 : 1 H_2/CO "synthesis gas."

When temperature and pressure in the reactor had stabilized, the catalyst charge pot was drained into the reactor and gas uptake was immediately

evident. The catalyst charge pot was rinsed into the reactor (as described above) 1 min after the initial charge. The extent of reaction was followed by tracking the pressure and temperature of a calibrated gas reservoir containing an excess of synthesis gas. When the desired amount of gas had been consumed, the reaction was quenched by quickly cooling the reactor and venting the synthesis gas. The reactor was then purged with nitrogen and opened to remove the polyaldehyde solution. The amount of toluene was reduced by rotary evaporation and the hydroformylated polymer was precipitated from the toluene by slow addition of methanol (500 mL) with stirring. The solvents were then decanted and the polymer redissolved with 500 mL of toluene and precipitated again with 500 mL of methanol. After decanting the solvents, residual methanol was removed from the polymer by rotary evaporation, leaving a light amber toluene solution of clean polyaldehyde. The extent of functionalization achieved was determined by comparing the integrals for the aldehyde groups and the residual olefin groups on the polymer in the ^1H-NMR.

Production of EPDM Polyol

A toluene solution of polyaldehyde was reduced in volume on a rotary evaporator and then placed in
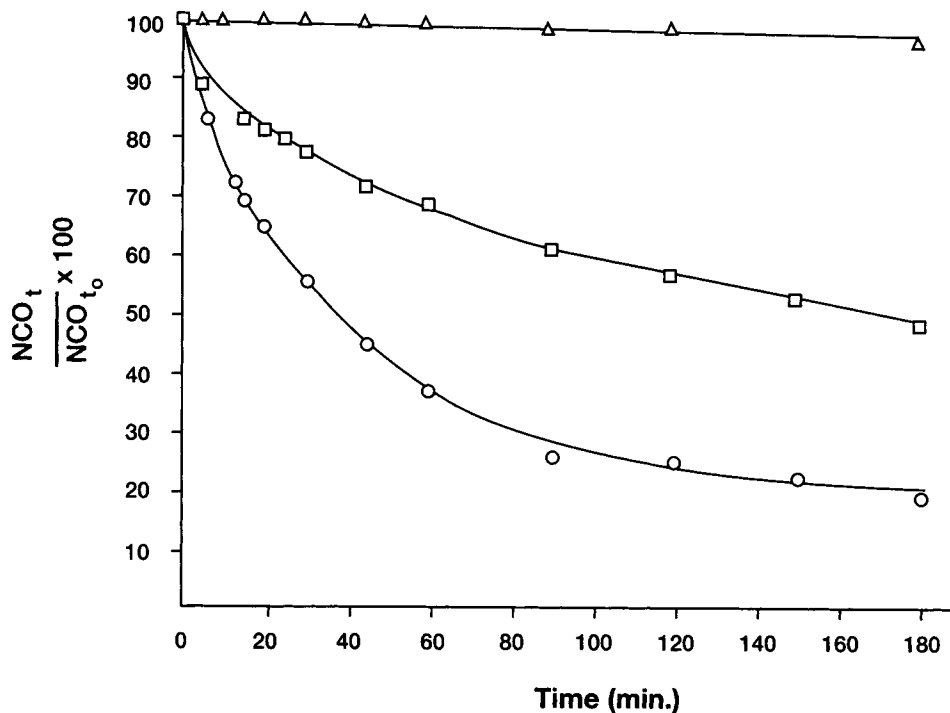
Figure 4 Reaction of phenyl isocyanate and various polyols in o-dichlorobenzene at 80°C. [phenyl isocyanate] = [polyol] = 0.16N. (△) PPG-2010 (polypropylene glycol; MN = 2000); (□) Commercial polybutadiene polyol R-45HT; (○) EPDM 3.7 OH/chain.

a silylated 4 L glass beaker. Tetrahydrofuran, 500 mL, and ethanol, 60 mL, were added to the solution. For 0.153 mol of aldehyde groups present in the polymer solution, 2.17 g (1.5 equiv., 0.0574 mol) of NaBH$_4$ were added slowly to the polymer solution. NaBH$_4$ was allowed to react for 18 h to ensure a complete reaction. The reaction was then quenched with 70 mL of 1.2M HCl in MeOH. This was allowed to stir for 30 min and then the polymer was precipitated with 350 mL of MeOH. The solvents were decanted and 250 mL of tetrahydrofuran was added to redissolve the polymer. An additional 10 mL of 1.2M HCl in MeOH was added to the solution to quench any remaining NaBH$_4$. The polymer was then precipitated with 350 mL of MeOH and the solvents were decanted. The polymer was then poured into a container made from Teflon-coated foil and dried in a vacuum oven at 40°C for 24 h. The extent of functionalization could be determined by comparing the integrals for the aldehyde groups and the residual olefin groups on the polymer in the ^{1}H-NMR.

Polybutadiene Polyaldehyde

A toluene solution of polybutadiene polymer was made by dissolving 350.70 g of polybutadiene in 600

mL of toluene and then degassing the solution with argon. In a separate capped bottle, Rh(acac)(CO)$_2$ (27.0 mg, 0.105 mmol) was dissolved in 100 mL of toluene and the solution was degassed by bubbling with argon. The reactor was charged and operated in the same manner as described for EPDM polyaldehyde.

Production of Polyol

The orange–amber, toluene solution of polybutadiene aldehyde was concentrated by rotary evaporation and placed in a 2 L beaker. To the polymer solution 500 mL of tetrahydrofuran and 70 mL of ethanol were added. NaBH$_4$ (3.2 g, 0.0846 mol, 1.45 equiv.) was added to the solution in portions. The solution immediately went from orange to bright yellow in color. The solution was left to stir overnight (18 h). The reaction was then quenched by bringing the solution to acidity with 70 mL of 1M HCl in ethanol. The polymer was then precipitated from solution with 500 mL of methanol. After decanting the solvents, the polymer was redissolved with 500 mL of tetrahydrofuran. The polymer solution was then reacidified with 10 mL of 1M HCl in ethanol and the polymer was precipitated with 500 mL of methanol. After the solvents were decanted, the polymer was redissolved in 500 mL of
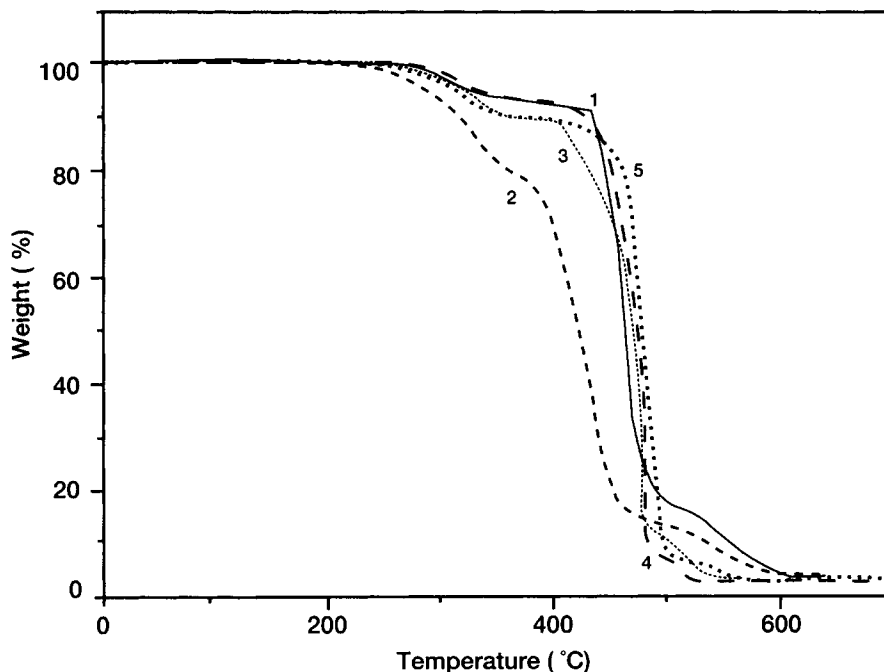
Figure 5 Thermogravametric analysis—polyurethane films made from various polyols:
1 (———) commercial polybutadiene polyol R-45HT; 2 (– – –) PTMO-2000; 3 (----) EPDM
3.7 OH/chain; 4 (— — — —) EPDM 2.5 OH/chain; 5 (· · · ·) EPDM 3.0 OH/chain.

toluene and residual methanol was removed by rotary evaporation. To further remove salts, the polymer solution was centrifuged and the polymer solution was decanted from the salts. The polymer was then precipitated from solution with 500 mL of methanol and solvents were decanted off. The remainder of the solvents were removed *in vacuo* to yield the neat material.

Simulated Melt-phase Hydroformylation

A sample of EPDM polymer (Nordel 1440) and the desired amount of Rh hydroformylation catalyst, either $HRh(CO)(PPh_3)_3$ or $Rh(acac)(CO)_2$, were dissolved in toluene in a dry box. The solution was mixed well and the toluene was removed by vacuum. The resulting thick film of the EPDM/catalyst was placed in a 30 mL Parr reactor in the dry box. The reactor was then removed from the dry box and heated to the desired temperature (150–215°C) in an oil bath under a CO/H_2 pressure of 1000 psig. The reaction was continued while maintaining a flow of CO/H_2 through the system to maintain a CO/H_2 molar ratio of about 1 : 1. The flow was measured at a pressure of about 1500 psig. Samples were removed at specified intervals and analyzed by FTIR and ^1H-NMR for aldehyde functional groups. The reaction conditions and results are set forth in Table II.

Production of Urethane Films

In a typical urethane formulation, the isocyanate was dissolved in 50 mL of *m*-xylene 24 h prior to use. The isocyanate solution was added to a solution containing the polyol, 1,4-butanediol (if the formulation called for it), and dibutyltin dilaurate in 50 mL of *m*-xylene. The dibutyltin dilaurate catalyst was added to the polyol/butanediol solution after complete dissolution of the polyol and the butanediol. The polyol/isocyanate solution was then vigorously mixed at room temperature for about 1 min. The solution was then poured into a Teflon-lined pan with dimensions 5.5 × 3.9 × 0.04 in. and placed into a standard oven at 95°C for 10–12 h. The thickness of the film varied from about 0.01 to about 0.025 in., depending on the percent solids of the polymer solution. The chemical structure of the films was studied by IR spectroscopy. In all cases, a strong carbonyl urethane group adsorption at 1720 cm^{-1} was observed. The isocyanate adsorption at 2270 cm^{-1} was not observed or was very weak, indicating that there was an essentially complete reaction.

CONCLUSIONS

Transition-metal-catalyzed functionalization of double-bond-containing polymers can produce

Table III Ultimate Strength and Elongation at Break of Urethane Formulations

Polymer	Hydroxy Groups	Equivalent Weight (g/mol —OH)	1,4-Butanediol	Ultimate Strength (psi)	Elongation (%)
EPDM 3.0	3.0 —OH/chain	1667	1 : 0	378.1	275.2
EPDM 3.0	3.0 —OH/chain	1667	1 : 1	513.0	209.3
EPDM 3.0	3.0 —OH/chain	1667	1 : 2	1278.0	190.1
EPDM 3.0	3.0 —OH/chain	1667	1 : 3	2332.0	166.0
EPDM 3.9	3.9 —OH/chain	1282	1 : 0	352.9	338.8
EPDM 3.9	3.9 —OH/chain	1282	1 : 1	1415.0	384.7
EPDM 3.9	3.9 —OH/chain	1282	1 : 2	2528.0	299.1
EPDM 3.9	3.9 —OH/chain	1282	1 : 3	2688.0	179.4
EPDM 5.0	5.0 —OH/chain	1000	1 : 1	1859.0	396.8
P(bd) 2.6	2.6 —OH/chain	1496	1 : 1	619	97
P(bd) 2.6	2.6 —OH/chain	1496	1 : 2	758	174
P(bd) 2.6	2.6 —OH/chain	1496	1 : 3	1238	154
P(bd) 7.6	7.6 —OH/chain	566	1 : 0	662	226
P(bd) 7.6	7.6 —OH/chain	566	1 : 1	1699	125
P(bd) 7.6	7.6 —OH/chain	566	1 : 2	2332	180
P(bd) 7.6	7.6 —OH/chain	566	1 : 3	2477	108
P(bd) 4.8	4.8 —OH/chain	854	1 : 0	314.2	40
R-45HT	2.3 —OH/chain	1203.4	1 : 0	189.0	100
R-45HT	2.3 —OH/chain	1203.4	1 : 1	425.0	238.0
PTMO-2000	2 —OH/chain	1000	1 : 1	587.4	1092

polyols that yield good properties when compared to terminally functional polyols and provide flexibility in areas that may be difficult to control by standard chain initiation–termination methods such as molecular weight, microstructure, and functional density. This chemistry provides control over both the amount of functional groups added to the polymer and the amount of double bonds left unreacted on the polymer backbone, which allows for greater control in optimization of the final product. By virtue of their greater thermal stability and hydrophobicity, these hydrocarbon-based polyols could have possible uses in the areas of thermally stable coatings, electronic potting compounds, cast elastomers, and sealants. Since the EPDM-based polyols have a saturated hydrocarbon backbone, these polyols could be used in applications where UV stability is desired.
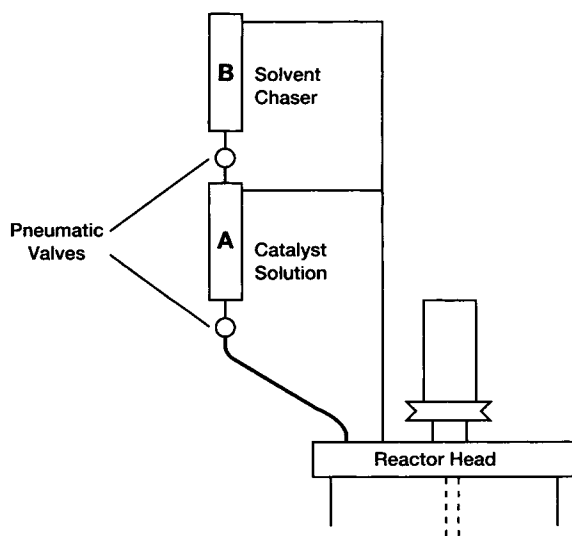
Figure 6 Catalyst addition system for 2L reactor.

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