

# Polymers from Renewable Sources. III. Hydroxy-Terminated Myrcene Polymers

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## Synopsis

A range of hydroxy-terminated polymyrcenes has been prepared using hydrogen peroxide initiated polymerization of pyrolysate grade,  $\beta$ -myrcene in *n*-butanol solution at 100°C. An oligomeric fraction, containing a large proportion of dimeric material formed via the Diels-Alder reaction, always accompanies the major polymeric fraction. Procedures are described for the removal of this oligomeric material. Polyols so prepared and purified had number average molecular weights ( $\bar{M}_n$ ) between 4000 and 2000 g mol<sup>-1</sup> at low and high initiator concentrations, respectively, with corresponding number average functionalities ( $\bar{f}_n$ ) between 1.3 and 2.3 and polydispersities ( $\bar{M}_w/\bar{M}_n$ ) of  $\sim 1.3$ . The microstructure of the polyols was investigated using NMR spectroscopy from which the main mode of propagation during polymerization of myrcene was deduced to be 1,4 addition across the conjugated double bonds. Glass transition temperatures of the polymyrcenes measured by differential scanning calorimetry were in the range -50--60°C.

## INTRODUCTION

Several classes of chemical compounds exist in sufficient abundance in nature for them to be considered as realistic potential sources of polymers. For example, in two previous papers<sup>1,2</sup> polyurethanes derived from furfural-based diisocyanates were described, and work is currently proceeding in these laboratories on liquid polyols derived from solid carbohydrate precursors.<sup>3</sup> The polymers described in this paper are hydroxy-terminated liquid rubbers, prepared by free-radical initiated polymerization of a readily available terpene, namely myrcene. These polyols may be regarded as analogues of the commercially available polybutadiene (PB) systems (which are used in polyurethane manufacture), but can be prepared using simpler experimental procedures. The new polyols may be similarly reacted with diisocyanates to yield polyurethanes.

$\beta$ -Myrcene<sup>1</sup> occurs in the free state in many natural oils, for example, those derived from hops and verbena.<sup>4</sup> Commercially, however, it is obtained by pyrolysis of  $\beta$ -pinene a major constituent of turpentine, which is a byproduct obtained from sulphite wood-pulping processes.<sup>5</sup> The pyrolysate contains  $\sim 80\%$  myrcene plus  $\psi$ -limonene ( $\sim 10\%$ ) and *l*-limonene ( $\sim 4\%$ ) and Diels-Alder dimers of myrcene. Myrcene can be regarded as a derivative of butadiene, as shown in Figure 1 in which the 2-methyl-2-penten-5-yl group is designated as R. Since myrcene is a conjugated diene it can undergo polymerization, and the preparations of free-radical,<sup>6</sup> cationic,<sup>6</sup> anionic,<sup>7</sup>

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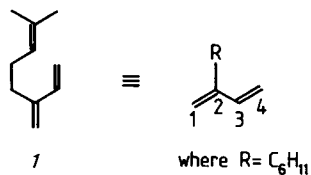


Fig. 1. Structure of myrcene.

and thermal initiated polymers have been reported. The products are generally gums or rubbers, and molecular weights are often low ( $< 30,000$ ), although polymers of high molecular weight ( $1.5 \times 10^5$ ) have been prepared using Ziegler-Natta catalysis.<sup>8</sup> The rubbery nature of these polymyrccenes suggests that hydroxy-ended polymers, liquid at room temperature could be prepared having similar properties to polybutadiene polyols. The preparation of PBs and hydroxy-ended polyisoprenes have been the subject of numerous publications and patents of which a useful bibliography is given by Brosse et al.<sup>9</sup> Generally, PBs are prepared by heating a mixture of butadiene, an alcohol as solvent/nonsolvent and aqueous hydrogen peroxide in a sealed vessel at temperatures above 90°C to cause fission of the hydrogen peroxide molecule into two hydroxyl initiator radicals. Initiation of polymerization then occurs largely by 1,2 addition, followed by chain propagation mainly via 1,4 addition of butadiene molecules with smaller amounts of 1,2 addition.<sup>10</sup> Termination of polymerization occurs mainly via radical coupling resulting in diols. Species with functionalities  $> 2$  are sometimes produced,<sup>11</sup> presumably by transfer reactions.<sup>12</sup>

A sealed reaction vessel is unnecessary for myrcene polymerization since the boiling point of myrcene (167°C) is well above that required to initiate polymerization when hydrogen peroxide is used as initiator. In common with PBs, a suitable solvent for myrcene and hydrogen peroxide is required, *n*-butanol was chosen and used for all experiments. A study was undertaken of the effect of reaction conditions on polyol properties. This allowed optimization of conditions to yield polyols suitable for polyurethane formation.

### EXPERIMENTAL

Myrcene (Aldrich, technical grade), was removed by vacuum, rotary-film evaporation from polymer residues (formed during storage by reaction of myrcene with atmospheric oxygen). The resulting myrcene was over 80% pure as assayed by GLC and was not purified further since the impurities, mainly limonenes, do not polymerize and are readily removed along with unreacted myrcene after the polymerization is effected. This is borne out by some studies in which fractionated myrcene [purity  $> 99\%$  (GLC)] was used and gave similar polyols.

In a typical polymerization, myrcene (300 mL) was mixed with *n*-butanol (200 mL), and the required quantity of 50% aqueous hydrogen peroxide in a 1 L flask equipped with a 1-m condenser and a nitrogen inlet. The mixture was purged with nitrogen for 30 min and then heated slowly (to avoid foaming) until it boiled gently under reflux ( $\sim 100^\circ\text{C}$ ). The solution was maintained at the reflux point for 7 h when conversions had essentially reached a maximum value, as optimized in preliminary experiments. The

volatiles, unreacted myrcene, its impurities, *n*-butanol, and water were removed by vacuum distillation at 100°C/10 mm. Dimers and other low molecular weight products were then removed by the following extraction technique. Crude polyol (100 g) was dissolved in 2-methyl butane (100 mL), and to this solution methanol (50 mL) was added. The mixture was shaken in a separating funnel and the lower layer containing the polyol and part of the methyl butane was run off and reextracted with two successive portions (50 mL) of methanol. The polyol solution was dried over anhydrous magnesium sulfate, and the volatiles were removed under vacuum after addition of quinone to prevent atmospheric oxidation.

The products were characterised by end-group analysis (acetylation)<sup>13</sup> to yield equivalent weight ( $\bar{E}_n$ ) data.  $\bar{E}_n$  is defined as the molecular weight per hydroxyl group present in the polymyrcenes or products extracted from them. Molecular weights ( $\bar{M}_n$  and  $\bar{M}_w$ ) were evaluated using gel permeation chromatography (GPC) and vapour pressure osmometry (VPO). GPC was performed at 23°C in THF (0.25% w/w solutions) using Sytragel columns (700–20000 Å, 500–2000 Å, 200–500 Å, 150–350 Å, 50–80 Å). Results were calculated relative to a poly(propylene oxide) (PPO) calibration. VPO measurements were made on a Knauer vapor pressure osmometer at 60°C in toluene solution. Calibration was effected with benzil and comparative studies on a commercial PBD, Arco R45-HT yielded an  $\bar{M}_n$  value of 2340 in good agreement with data reported by Ono et al.<sup>11</sup> Infrared spectra (IR) were recorded on a Perkin-Elmer Spectrophotometer Model 710b from liquid films between NaCl plates. Proton nuclear magnetic resonance (NMR) spectra were recorded on a Perkin-Elmer R34 instrument at room temperature from 20% solutions in carbon tetrachloride, with tetramethyl silane as internal standard. Spectra were recorded at 220 MHz with multiple integration<sup>5</sup> to facilitate measurement of the integral step heights for compositional analysis of the microstructure of the various polyols prepared.

GLC studies were performed on a Hewlett-Packard 5830a machine with 10% Carbowax 20M on Chromosorb W, 80–100 mesh packing in the column (2 mm ID × 1 m). The oven temperature was held at 80°C for 10 min and then raised at 10°C min<sup>-1</sup> to 200°C.

Glass transition temperatures ( $T_g$ ) were measured on a Dupont 900 Thermal Analyzer with a DSC attachment. Samples (~10–15 mg) and an inert reference, glass beads (10 mg), were sealed in aluminium pans and cooled from room temperature to -150°C and then heated at 20°C min<sup>-1</sup> to a maximum temperature of 50°C.

## RESULTS AND DISCUSSION

Table I lists details of the liquid myrcene polymers (PM) prepared on the small scale to optimize preparative conditions to product a PM on a larger scale having a functionality of ~2.0 for subsequent polyurethane formation.

### IR Analysis

The work-up procedure employed removes myrcene as shown in Figure 2, where IR spectra of myrcene and a typical polymyrcene (A3) are compared. The strong C=C absorption present at 1600 cm<sup>-1</sup> in myrcene (due

TABLE I  
 Polymyrcene Preparations

Myrcene (mL)	[H <sub>2</sub> O <sub>2</sub> ] (wt %)	Polymer code	Appearance
30	0.5	A1	Colorless, hazy viscous liquid
30	1.0	A2	
30	1.9	A3	Pale yellow hazy viscous liquid
30	3.6	A4	
30	5.4	A5	
300	2.8	B1	Colorless, hazy viscous liquid
300	2.8	B2	

to 1,4 diene) is absent in polymer A3 which also shows a broad absorption at  $\sim 3400\text{ cm}^{-1}$  from the hydroxyl groups. The general appearance of the spectrum of A3 is very similar (except for the presence of the OH absorption) to that found by Sivola<sup>7</sup> for a polymyrcene prepared anionically in benzene. Free-radical polymerization of myrcene could involve propagation in three distinct ways resulting in the repeating units shown in Figure 3. Two of the units possess pendent groups which give rise to IR absorptions of diagnostic value. Thus the pendent vinyl group in the 1,2 repeat unit would produce sharp absorptions at 3090 (CH str.), 1010, 910  $\text{cm}^{-1}$  (CH<sub>2</sub> out of plane def.) Figure 2 shows these bands to be almost absent. The pendent vinylidene group in 3,4 units would give rise to bands at 3040 (CH str.), 1670 (double bond str.), and 900  $\text{cm}^{-1}$  (=CH<sub>2</sub> wag): All these bands are clearly visible in the spectra of the A-series of PMs. This suggests that 1,2 addition is not present in significant amounts, but that 1,4 addition is possibly the most important mode of propagation in these systems. However, a clearer picture of the microstructure of these polymers can be gained from NMR studies.

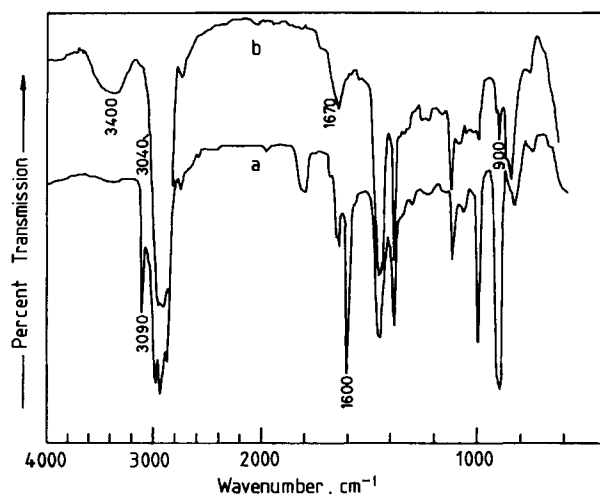


Fig. 2. Infrared spectra of (a) myrcene and (b) a hydroxy-terminated polymyrcene A3.

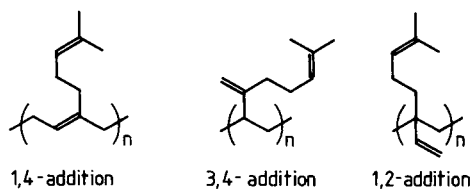


Fig. 3. Repeat units in polymyrcene.

### Microstructure of PMs from NMR Analysis

Sivola<sup>7</sup> has used proton NMR at 60 MHz to study the microstructure of polymyrcene prepared by anionic initiation. The following assignments (Table II) were established for the chemical shifts of the various protons present in the possible repeat units in the polymyrcenes.

The polymyrcenes, prepared using hydrogen peroxide initiation in the present studies, were investigated using proton NMR at 220 MHz, and a typical spectrum is shown in Figure 4 for polymer A3. All the resonances observed by Sivola are present, but it can be seen that the olefinic protons associated with 1,2 and 3,4 addition at 1.3 and 4.7 ppm give rise to very small peaks. The hydroxyl protons were not detected by loss of a signal when the spectrum was shaken with D<sub>2</sub>O, possibly due to their low concentration and the breadth of the hydroxyl adsorption.

TABLE II  
NMR Analysis of Polymyrcene<sup>7</sup>

Proton type		Chemical shift ( $\delta$ ) (ppm)	Designation in Fig. 4
Methyl		1.6, 1.65	D
Methylene (adjacent to $-\text{CH}_2-$ )		2.0	C
Methylene (adjacent to $-\text{CH}-$ )		1.3-1.35	E
Methine		2.1	C
Olefinic <sup>a</sup>	<u>H</u>	5.0	A
	<u>H</u>	4.7	B
	<u>H</u>		
	H <u>H</u>	5.6	—
	H <u>H</u>		
	<u>H</u> H	4.7,5.0	A,B
	<u>H</u> H		

<sup>a</sup>Proton responsible for signal underlined.

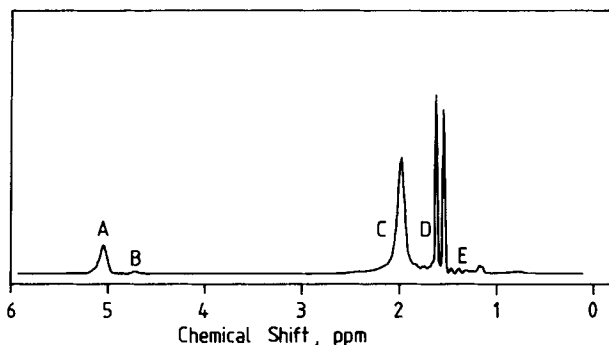


Fig. 4.  $^1\text{H-NMR}$  spectrum of polymyrcene polyol A3. Chemical shifts are on the  $\delta$  scale; A-E refer to protons cited in Table II.

Sivola has derived equations to calculate the various extents of 1,2, 1,4, and 3,4 structures in his polymers. His analysis, however, suffers from two major sources of error. First, it uses resonances due to B and E protons, whose small size (Fig. 4) magnifies errors in measurement of step heights, and, second, the equations derived overcount the protons actually present.

Equations can be derived to analyze the microstructure of these polymers which involve the larger step height associated with signals from A, C, and D protons. There are two approaches which can be used. The first assumes that the amount of 1,2 structure present is negligible. IR (absence of absorptions at 3090, 1010, and 910  $\text{cm}^{-1}$ ; discussed earlier) and NMR (absence of a signal at  $\delta = 5.6$ ) indicate that the 1,2 content is below the limits of detection of the measuring instruments employed in this study.

Equations can be derived for the 1,4 and 3,4 contents in the following manner: The six protons giving signals at  $\delta = 1.6\text{--}1.65$  designated D in Table II and Figure 4 are present in both structures and may be used as a reference signal. If the mole fraction of 3,4 units present is defined as  $x$  and that due to 1,4 units as  $y$ , then the ratio of D:A protons is given by the expression

$$\frac{D}{A} = \frac{6}{2y + x} \quad (1)$$

Similarly, the ratio of D:C protons is given by the expression

$$\frac{D}{C} = \frac{6}{8y + 5x} \quad (2)$$

Since  $x + y = 1$ , then the equations may be solved to give two routes to  $x$ , i.e.,

$$x = \frac{2D - 6A}{D} \quad (3)$$

or

$$x = \frac{8D - 6C}{3D} \quad (4)$$

and  $y = 1 - x$ . Taking the arithmetic mean of (3) and (4) yields

$$x = \frac{7D - 9A - 3C}{3D} \quad (5)$$

The data obtained using this approach and eq. (5) are presented in Table III.

The alternative approach derives equations assuming 1,2 structures to be present. In this derivation, the mole fraction of 1,2 structure is defined as  $z$ . Using a similar approach to that described previously, the 6D protons can still be used as a reference since they are also present in the 1,2 structural unit. Using the ratio D:A and D:C leads to expression for  $x$  and  $y$ , respectively, as

$$x = \frac{2D - 6A}{D} \quad (6)$$

and

$$y = \frac{3C - 4D + 9A}{3D} \quad (7)$$

No further expressions using the larger step-heights from A, C, and D protons can be evaluated.

However, when this approach is used,  $z$  is evaluated as a negative number. This may arise from:

- (a) errors associated with step-height measurement;
- (b) the assumption that only 1,2, 1,4, and 3,4 structural units are present;
- (c) the assumption that there are negligible contributions from oligomeric species present in the polymer (these species are described and discussed in the next section).

The data presented in Table III indicate that the 1,4 structure predominates as would be expected on steric grounds for a 2-substituted butadiene. The initiator concentration has little effect upon the microstructure of these polyols; the larger scale preparations may have a slightly altered composition.

TABLE III  
Microstructure of Myrcene Polyols

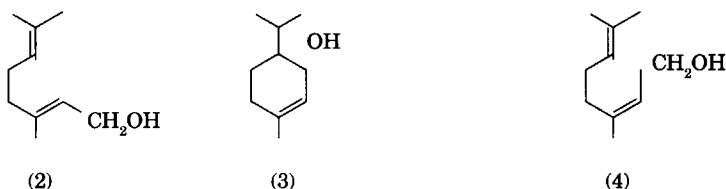
Polymer code	% 1,4	% 3,4
A1	84	16
A2	83	17
A3	79	21
A4	85	15
A5	85	15
B1	77	23
B2	77	23

### Molecular Weight and Functionality

In preliminary studies, the workup procedure involved distillation of volatiles at 100°C/0.1 mm Hg rather than the extraction procedure described in the Experimental sections. The former process was found to be inefficient, removing only the major proportion of unreacted myrcene and some low molecular weight hydroxy compounds. GPC and VPO data on systems produced in this way showed considerable discrepancy between the  $\bar{M}_n$  values obtained. Figure 5 shows comparative GPC traces for a polyol subjected to removal of volatiles by distillation and after an extractive workup procedure.

A discrete peak can be seen in the vacuum stripped sample at high elution volumes (225), i.e., low molecular weight which has almost disappeared in the extracted sample. Since it is not possible to effect complete removal of oligomer, traces are found in the extracted samples as shown in Figure 6.

After drying the methanol extract solution, the extracted material can be obtained as a clear, colorless liquid with a geraniumlike odour after removal of the methanol. The extracted material has an  $\bar{E}_n$  value of 258 and  $\bar{M}_n$  value of 232 (GPC) giving a number average ( $\bar{F}_n = \bar{M}_n/\bar{E}_n$ ) functionality of 0.9. GLC analysis of this fraction at 200°C showed the presence of at least 30 volatile components, of which three were identified as geraniol,<sup>2</sup> terpineol,<sup>3</sup> and nerol.<sup>4</sup>



However, 2,3, and 4 account for only 4% of the material eluting from the chromatography column. The major peaks associated with the unidentified components had retention times in excess of those of the terpene alcohols and two of these peaks accounted for ~32% of the total volatile material. Hayashi and Komae<sup>14</sup> have identified four myrcene dimers<sup>5-8</sup> as the main compounds formed in the dimer fraction by thermal polymerization of myrcene at temperatures below 190°C.

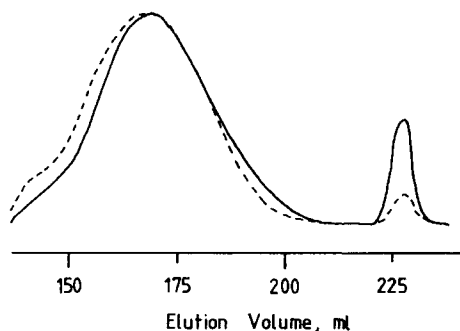


Fig. 5. GPC traces showing the effect of workup procedure on polymyrcene polyols: (—) distillation; (---) extraction.



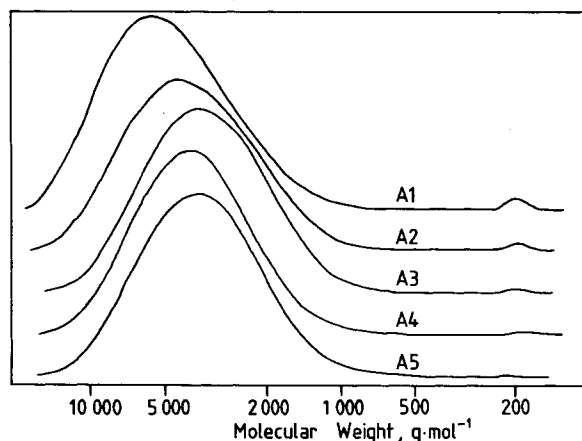
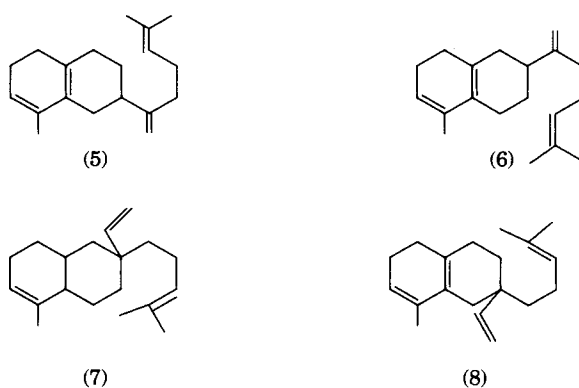


Fig. 6. GPC traces of polymyrcene polyols after extraction. Molecular weights are relative to a PPO calibration.



Such compounds are formed by a Diels–Alder, multicenter reaction, and the dimers dissociate at higher temperatures, leading to polymyrcene. Such compounds would be expected to form under the conditions employed in these studies especially at low initiator concentrations. Thus the larger oligomer peaks seen in the GPC traces (Fig. 6) for sample A1 and A2 may arise in part from such reactions.

Data obtained by VPO and GPC for the PM's are presented in Table IV and Figures 7(a) and 7(b). Similar data were obtained for Arco R45-HT

TABLE IV  
Polymyrcene: Molecular Weight and Functionalities

Polymer	[H <sub>2</sub> O <sub>2</sub> ] (% w/w)	$\bar{f}_n$	$\bar{M}_n$	$\bar{f}_n$ (VPO)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$ (GPC) <sup>a</sup>	$\bar{f}_n$
A1	0.5	3185	4030	1.26	4140	5600	1.35	1.30
A2	1.0	2255	3410	1.51	3410	4600	1.35	1.51
A3	1.9	1906	3270	1.72	3010	3990	1.33	1.58
A4	3.6	1626	3750	2.30	3470	4600	1.32	2.14
A5	5.4	1345	3100	2.30	3120	4130	1.33	2.32
B1	2.8	1322	2110	1.60	2950	4100	1.39	2.23
B2	2.8	1412	2080	1.47	2810	3850	1.37	1.99

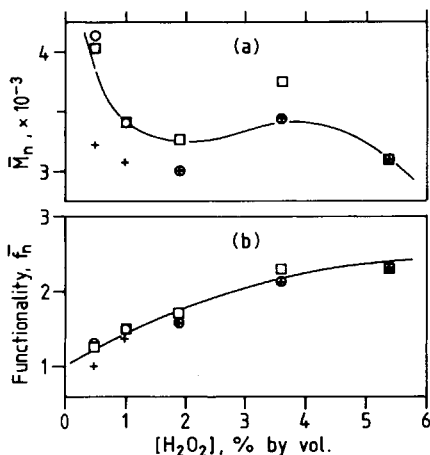


Fig. 7. Effect of initiator concentration in (a) molecular weight ( $\bar{M}_n$ ) and (b) functionality ( $\bar{f}_n$ ) of polymyracene polyols: (□) VPO; (+) GPC including oligomer fraction; (○) GPC excluding oligomer fraction.

which gave values for  $\bar{M}_n$  (VPO) 2343,  $\bar{M}_n \bar{M}_w$ ,  $\bar{M}_w/\bar{M}_n$ , (GPC) 2919, 4965, 1.7, leading to  $\bar{f}_n$  (VPO) = 2.2,  $\bar{f}_n$  (GPC) = 2.7, assuming the equivalent weight to be 1088 as obtained by acetylation. These results, although in accord with data produced by Ono<sup>11</sup> on a similar ARCO R45-HT system, show the disparity in values obtained by the two methods of measurement.

In the PM A-Series in Table IV, increasing the initiator concentration yields polymers of low equivalent and molecular weights, the equivalent weight being more drastically affected possibly due to the extraction of a low molecular weight "tail" from the polymer fraction along with extraction of oligomer. Evidence may be cited for such behavior (see Fig. 8) where GPC clearly shows the presence of oligomer and low molecular weight polymer in the extracted material from the PM, (B1). The peak at the right corresponds to that in Figure 5 at  $\sim 225$  mL and that at  $\sim 200$  g mol<sup>-1</sup> in Figure 6. The broad peak (Fig. 8) corresponds to extracted material of relatively low  $\bar{M}_n \approx 800$ .

Functionality (Table IV) increases from 1.3 to about 2.3 in the initiator concentration range studied. Although the VPO data should be more reliable, some uncertainty in the  $\bar{M}_n$  values obtained must arise when the

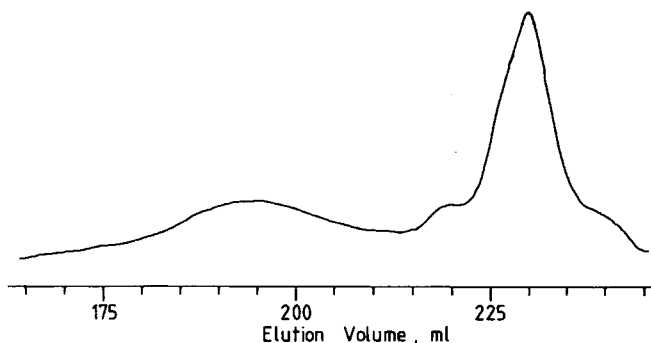


Fig. 8. GPC trace of methanol-soluble extract from a polymyracene polyol.

slightly volatile oligomer is still present in the polymer (i.e., PMs A1 and A2). Since  $\bar{f}_n$  increases as  $[\text{H}_2\text{O}_2]$  increases, this suggests that transfer reactions involving hydrogen abstraction from allylic sites on the diol polymers occur, followed by radical coupling leading to polyfunctional material.

The polydispersity index,  $I = \bar{M}_w/\bar{M}_n$ , varies little with  $[\text{H}_2\text{O}_2]$  and at  $1.33 \pm 0.03$  (excluding any contribution from the oligomer fraction) suggests a relatively narrow distribution.

Further evidence for the functionality data was obtained from studies of polymer formation in bulk with di(isocyanato-phenyl) methane (MDI) at 70°C using a 4% excess on the calculated stoichiometric equivalence of hydroxyl and isocyanate groups. The polyurethanes formed were cross-linked rubbers. However, the preparative conditions used with gel times ranging from less than 1 h for A5 to about 16 h for A1 are not stringent enough to promote crosslinking via allophanate formation. Crosslinking must therefore arise from polyol species having functionalities greater than 2.0, although it is obvious from the  $\bar{f}_n$  values (Table IV) that these PMs must also contain monofunctional material.

### Polymer Yields

Conversion increases with increasing  $[\text{H}_2\text{O}_2]$  (Fig. 9), but a significant amount of the myrcene is converted to oligomeric material. Thus for B1 the initial conversion of 59% was reduced to 50% on removal of oligomer. As  $[\text{H}_2\text{O}_2]$  increases the proportion of extractable material also increases, presumably because of its lower equivalent weight and increased polarity which facilitates solubility in methanol.

### Glass Transition Temperatures

Since  $T_g$  values of polybutadiene diols are generally about  $-80^\circ\text{C}$ , it would be expected that a substituted butadiene formed mainly by via 1,4 propagation, would have a  $T_g$  higher than  $-80^\circ\text{C}$  but still below room temperature. The  $T_g$  values for the PM series of polymers are plotted vs. equivalent weight in Figure 10. The values ( $-60$ – $-50^\circ\text{C}$ ) reflect the steric hindering effects of the  $\text{C}_6$  side chains on segmental motion. The initial decrease in  $T_g$  with increasing equivalent weight reflects the decrease in end-group

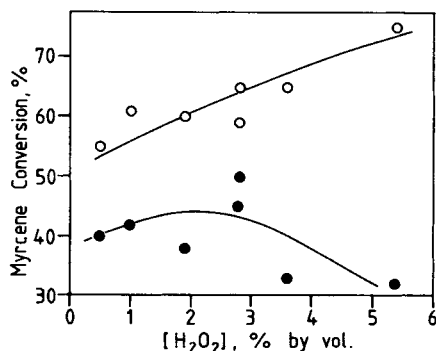


Fig. 9. Effect of initiator concentration on myrcene conversion: (○) overall conversion including oligomer; (●) conversion after oligomer removal via extraction.

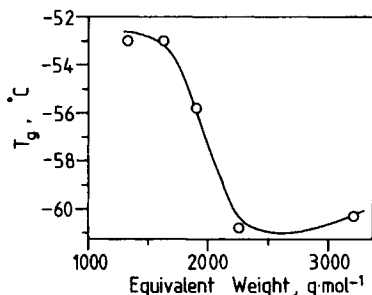


Fig. 10 Glass transition temperatures of polymyrcene A-series polyols.

concentration, thereby reducing the extent of hydrogen bonding possible between hydroxyl substituents and thus allowing greater chain mobility.

### Polyols from Other Terpenes

Some other commercially available terpenes were also screened as precursors for liquid rubber formation under similar conditions to those described for myrcene. The results of such studies are summarized in Table V.

Of the terpenes screened, only ocimene showed promise as a potential polyol: This is expected since ocimene has a diene structure similar to that of myrcene,<sup>4</sup> whereas the others are in effect hindered vinyl monomers.

### CONCLUSIONS

This study has demonstrated that hydroxy-terminated polymers can be prepared from certain terpenes provided that these contain the butadiene nucleus. Such compounds produce liquid rubbers of moderate molecular weight by reactions which can be carried out at atmospheric pressure in contrast to the use of gaseous butadiene in pressure vessels. Polymers may be prepared having functionalities ( $\bar{f}_n$ ) of  $\sim 2.0$ , which implies the poly-

TABLE V  
Attempted Polyol Formation from Terpenes

Terpene (source)	Conversion <sup>a</sup> (%)	Product	Approx. $M_n$
Carvone (Aldrich)	12	Brown glass	<1000 <sup>b</sup>
$\alpha$ -Ocimene (Bush-Boake-Allen)	30	Stiff, pale —yellow syrup	$\sim 1000^b$
Dipentene (BDH)	14-17	Mobile colorless oil	200 <sup>c</sup>
$\alpha$ -Pinene (BDH)	14	Very viscous pale yellow liquid	400 <sup>b</sup>

<sup>a</sup> From weight of product after removal of volatile components.

<sup>b</sup> Estimated by IR spectroscopy from ratio OH/CH adsorptions.

<sup>c</sup> Estimated from GPC.

merization mechanism is similar to that for polybutadiene. Conversions are relatively high in short reaction times when pyrolysate grade myrcene is employed without further purification.

A route therefore exists for the conversion of wood-pulping byproducts into liquid rubbers, and thence into polyurethanes with potential applications as elastomers, adhesives, sealants, foams, and potting compounds. Further papers in this series will report studies on such polyurethane materials.

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