

# Preparation and Characterization of Lactitol-Based Poly(ether polyol)s for Rigid Polyurethane Foam

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## SYNOPSIS

Propoxylation of lactitol [4-*O*- $\beta$ -D-galactopyranosyl-D-glucitol] under alkaline conditions afforded poly(ether polyol)s (PEP) which have been characterized by their unsaturation content, alpha color, hydroxyl number, viscosity, hygroscopicity, and molecular weight distribution. The analogous sucrose-based PEP were prepared for comparison. Lactitol was found to require shorter reaction times and produced lighter-colored polyols than did sucrose. Polyols produced from lactitol displayed similar physical properties to sucrose-based PEP. Molecular weight analysis by GPC using the universal calibration method showed lactitol PEP to have polydispersities between 1.04 and 1.07. Negligible decomposition of lactitol during propoxylation was confirmed by <sup>13</sup>C-NMR and GPC. <sup>1</sup>H-NMR of trifluoroacetyl derivatives of lactitol PEP afforded secondary determination of  $M_n$ . In addition, rigid polyurethane foams (PURF) formulated with lactitol-, sucrose-, or commercial sucrose-glycerin-based polyols and PAPI 27 were prepared and characterized. Lactitol-based PURF were found to compare favorably with sucrose-based foams, displaying a density and compressive strength of 28.9 kg/m<sup>3</sup> and  $1.213 \times 10^6$  N/M<sup>2</sup>, respectively. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polyurethanes derived from poly(ether polyol)s (PEP) represent a class of highly versatile and commercially important synthetic polymers.<sup>1,2</sup> Production of polyols suitable for low-density rigid polyurethane foam (PURF) typically involves alkaline-catalyzed high-temperature alkoxylation of polyhydroxy compounds having functionality ( $f_n$ )  $\geq$  4.<sup>3</sup> Although the high functionality and the low cost of carbohydrates make them ideal candidates for PEP formation, non-reducing sugars appear to be most practical because alkoxylation of reducing sugars under alkaline conditions frequently results in browning products possessing reduced hydroxyl functionality. Removal of the aldehyde or potential aldehyde group of mono- and disaccharides by reduction and glycoside formation, respectively, is known to increase heat and alkaline stability.<sup>4</sup> In

an effort to explore the utilization of lactose, a high-volume side product of the dairy industry, lactitol (reduced lactose), is currently under investigation in our laboratory as a basis for PURF-suitable PEP. Direct propoxylation of lactose [4-*O*- $\beta$ -D-galactopyranosyl-D-glucose], a reducing sugar, was carried out by Viswanathan et al., and the resulting polyols were used to prepare PURF.<sup>5</sup> However, these polyols demonstrated unusually low viscosity and considerably more caramelization (e.g., decomposition) than did analogous sucrose-based PEP.<sup>6,7</sup>

Alkoxylation of lactitol [4-*O*- $\beta$ -D-galactopyranosyl-D-glucitol] was carried out previously, and the resulting PEP was used to make surfactants<sup>8</sup> and PURF<sup>9</sup> by a two-step prepolymer method. No reports of lactitol-based PURF prepared by a single-step protocol using polymeric isocyanates have yet appeared. Moreover, the physical properties of lactitol-based PEP have not been reported in significant detail.

In this article, we report the synthesis and characterization of 2-hydroxypropyl adducts of lactitol. Homologs having from 1 to 3 propylene oxide (PO)

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moieties per hydroxyl were prepared by reaction of lactitol dihydrate with PO under alkaline conditions. Analogous sucrose-based PEP were prepared similarly. Sucrose, a nonreducing sugar, is a well-established initiator for PEP. Thus, it provides a good benchmark whereby lactitol can be evaluated. Comparison of initiator reactivity as well as the physical properties of the respective PEP by standard methods provides information critical to evaluating the efficacy of using lactitol for commercial PEP manufacture. Preparation of PURF by the reaction of lactitol PEP with polymeric isocyanate PAPI 27 in a single-step protocol afforded low-density foams that were compared with analogous sucrose- and voranol-based PURF.

## EXPERIMENTAL

### Polyol Preparation

Propylene oxide (PO) (Fisher Scientific) was dried by passage through a column of activated 4 Å molecular sieves immediately prior to use. The catalysts KOH, triethylamine (TEA), and potassium *tert*-butoxide (*t*-BuOK) (Aldich Chemical, Milwaukee, WI) were used as received. KOH was assumed to contain 15% (w/w) water. Lactitol polyols were prepared by reacting 150 g lactitol dihydrate (provided as a gift from Purac, U.S.A., and Mitsubishi, Japan) with the appropriate amount of basic catalyst and anhydrous PO. Water contained in the mixture was treated as a difunctional initiator. Thus, 13 equivalents of PO were used to achieve a PO to hydroxyl ratio (PO/OH) of 1, 26 equivalents PO for PO/OH = 2, and 39 equivalents for PO/OH = 3. The reaction mixture was placed in a 1 L high-pressure vessel (Autoclave Engineers, Erie, PA) equipped with a motorized stirrer. The system was sealed and purged three times with dry N<sub>2</sub> to reduce the risk of oxidative degradation and/or explosion. Reactions were run at 110°C with constant stirring (800 rpm) and terminated when the pressure, due to unreacted PO, had dropped and stabilized. Anhydrous sucrose was reacted similarly, but with the addition of two equivalents of water to simulate as much as possible the lactitol initiator system. The polyols were diluted with acetone and quenched with Amberlite IR-120(H<sup>+</sup>) to neutrality, then decolorized with Darco G-60 (5% w/w of polyol). Acetone and unreacted PO were removed under reduced pressure. Commercial sucrose-glycerin-based polyols (Voranol 800, 490, 446, 370, 360) were obtained from Dow Chemical (Midland, MI).

### Polyol Characterization

<sup>1</sup>H-NMR spectra were recorded on a QE-300 instrument (General Electric, NMR-Instruments, Fremont, CA) operating at 300 MHz. For <sup>13</sup>C-NMR measurements, the QE-300 was operated at 75 MHz in an NOE suppression mode (D5 set to 10 s). IR data were recorded using a Galaxy 3000 FTIR (Mattson, Madison, WI) using neat samples between NaCl plates. Hydroxyl number, unsaturation, and alpha color were determined according to ASTM methods D4274-88, D4671-87, and D4890-88, respectively. Viscosity was determined using a controlled stress rheometer (Carri-Med, Ltd., Dorking, England) with a 2 cm disc having a 4° pitch and 110 μm truncation.<sup>†</sup> The moisture absorption properties (hygroscopicity) of the polyols were determined by placing dried 2 g samples in small Petri dishes inside a sealed chamber having a reservoir of saturated Mg(NO<sub>3</sub>)<sub>2</sub>. The chamber was placed in a conditioning room with an average temperature of 25.7°C. At this temperature, the relative humidity inside the chamber was assumed to be 52.8%.<sup>10</sup> Masses were taken at 24-h intervals to assay the relative mass increase due to water absorption.

### Molecular Weight Measurements

Lactitol PEP was purified by preparative gel permeation chromatography (GPC) prior to molecular weight analysis. Lower-weight copolyols were removed by eluting the mixture as a 10% (w/w) aqueous solution through a 30 × 2 cm column packed with 45 μm Toyopearl HW-40F (TosoHaas, Montgomeryville, PA) and using water as the mobile phase at 0.37 mL/min. Detection was accomplished by an on-line differential refractometer (DRI) (Waters R-403, Waters, Assoc., Milford, MA). Molecular weight measurements were accomplished by GPC using two columns in series (50 + 100 Å PLgel, Polymer Laboratories, Amherst, MA) and on-line DRI-viscometry detection (Viscotek Corp., Houston, TX) with 0.45 μm filtered THF (certified grade, Adrich Chemical) as the mobile phase at 1 mL/min. Samples were injected at a concentration of ~ 4 mg/mL via a 100 μL loop. Molecular weight distributions were calculated from a universal calibration curve [Log(IV × MW) vs. RV] based on narrow polystyrene standards (Pressure Chemical, Pittsburgh, PA) using Viscotek TriSEC software (Viscometry module, Version 2.60). For secondary de-

<sup>†</sup> We wish to thank Dr. Charles Shoemaker, Food Science and Technology, University of California, Davis, for use of the instrument.

**Table I** Typical Foam Formulation

Component	Part by Weight
Polyol <sup>a</sup>	100
Genetron 141b	35
DABCO R-8020	1.8
DABCO DC-193	1.5
PAPI 27	(105–110) <sup>b</sup>

<sup>a</sup> Dow voranol 446(OH# = 438); lactitol PEP(OH# = 420.3).

<sup>b</sup> Isocyanate to attain index of 105.

termination of  $M_n$  via  $^1\text{H-NMR}$ , trifluoroacetyl (TFA) derivatives of purified lactitol-PEP were prepared according to ASTM 4273-83, method A.

### Foam Preparation

PURF were prepared by adding PAPI 27 (polymeric diphenylmethane diisocyanate, equivalent weight 134; Dow Chemical, Midland, MI) to a premix of PEP, DABCO R-8020 (amine catalyst; Air Products and Chemicals, Allentown, PA), surfactant DABCO DC-193 (silicone-glycol copolymer; Air Products and Chemicals), and blowing agent Genetron 141b (dichlorofluoroethane; Allied Signal, Morristown, NJ) in ratios given in Table I. The combined materials were mixed in a 16 oz paper cup for 10 s using a Barnant mixer (Series 10, Model 700-5400; Barnant Co., Barrington, IL) equipped with a turbine rotor (Model 4544-10 : 2 in. diameter,  $\frac{3}{8}$  in. bore) at 2500–3000 rpm, then quickly poured into a 13 × 16 × 16 cm wooden mold which had been coated with wax. Foams were allowed to rise freely under ambient conditions, then removed from the mold and cured 24 h at room temperature and ambient humidity.

### Foam Characterization

The foams were cut into 4 × 4 × 5 cm test samples with a band saw and all specimens conditioned for 48 h at 21°C and 65% relative humidity prior to characterization. Apparent core densities were determined by a caliper and analytical balance. The compressive properties were measured in accordance with ASTM D1621-73 using an Instron 1122 (Instron Corp., Canto, MA) with a full-scale load of 50 kg and a crosshead speed of 5 mm/min.

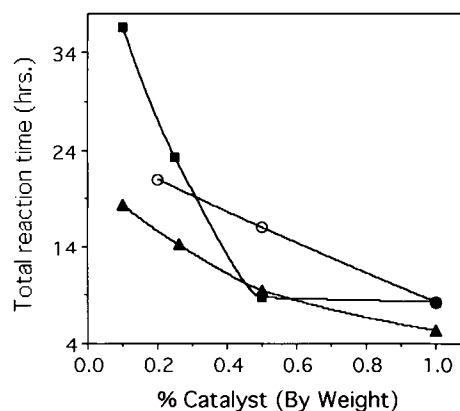
## RESULTS AND DISCUSSION

### Effects of Catalyst Type and Amount

Lactitol and sucrose were propoxylated using varying amounts of the catalyst to probe the effect of base type and amount upon total reaction time, alpha color, and unsaturation of the resulting PEP. Figure 1 shows the decrease in the total reaction time required for monopropoxylation (PO/OH = 1) of lactitol using KOH, TEA, and *t*-BuOK. Most notable are the shorter reaction times associated with KOH. While similar decreases in reaction time with increasing base amount were also noted for monopropoxylation of sucrose, reaction times tended to be longer overall than for lactitol (Table II). The apparent lower reactivity of sucrose could be attributed to less homogeneity than in the lactitol system; sucrose remains a solid at the reaction temperature while lactitol dihydrate melts at 76–78°C. Evidence of solid-phase reaction dynamics was corroborated by the observation that propoxylations run with coarsely ground sucrose required significantly longer reaction times than did those run with finely pulverized sugar. An analogous dependence on mesh size was not as pronounced with lactitol.

Alpha color, a rough measure of the extent of caramelization, was considerably lower for lactitol-based PEP than for sucrose PEP. Presumably, decomposition does not occur as much in the former. This is in contrast to the deep red color of lactose-based polyols reported by Viswanathan et al.<sup>5</sup> Removal of the aldehyde group has apparently blocked or significantly slowed the browning pathway.<sup>11</sup>

The effect of base concentration on unsaturation content appears to vary among catalysts. While an increase in the percentage of KOH or *t*-BuOK



**Figure 1** Reaction time for propoxylation of lactitol (PO/OH = 1, 110°C) using various catalysts: (▲) KOH; (○) triethylamine; (■) *t*-BuOK.

**Table II** Effect of Base Type and Amount on Reaction Time<sup>a</sup> and Color of Polyol

Type of Catalyst	% Base <sup>b</sup>	Sucrose		Lacitol	
		Reaction Time (h)	Alpha Color <sup>c</sup>	Reaction Time (h)	Alpha Color <sup>c</sup>
KOH	1.0	4.75	300	5.4	40
KOH	0.6	12.5	500	9.5	40
KOH	0.26	19	> 500	14.2	15
TEA <sup>d</sup>	2.0	8	> 500	10	40
TEA	1.0	11	> 500	8.3	35
TEA	0.26	46	> 500	21	15
<sup>t</sup> BuOK <sup>e</sup>	1.0	15	> 500	8.3	100
<sup>t</sup> BuOK	0.51	14	> 500	8.7	150
<sup>t</sup> BuOK	0.25	24.3	> 500	23	30

<sup>a</sup> For propoxylation using a stoichiometric ratio of PO/OH = 1.

<sup>b</sup> Percent by weight of initiator.

<sup>c</sup> After decolorization with Darco G-60.

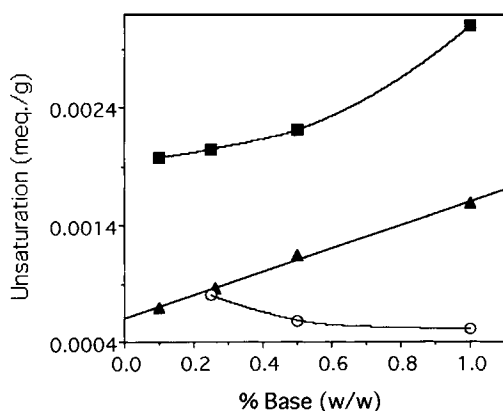
<sup>d</sup> TEA = triethylamine.

<sup>e</sup> <sup>t</sup>BuOK = potassium *tert*-butoxide.

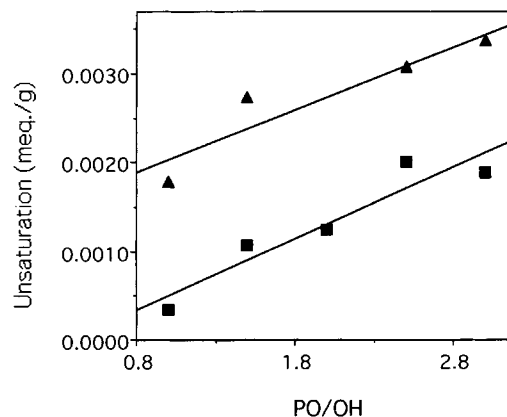
caused a notable elevation of unsaturation in the polyols, TEA appeared to have little influence on unsaturation (Fig. 2). Alkaline earth hydroxides and alcoholates are known to affect unsaturation via concomitant activation- $\beta$ -elimination of PO [Scheme (1)] in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ , with increasing metal ( $M^+$ ) concentrations leading to higher levels of unsaturation.<sup>12,13</sup> That elimination was most dominant with *t*-BuOK was evidenced by the higher levels of unsaturation obtained with this catalyst.<sup>14</sup> The results for TEA are not as readily explained. Although trialkylamines are commonly involved in polyol manufacture,<sup>15</sup> we are unaware of any reports addressing the kinetics of propoxylation under amine catalysis.

Lactitol-based polyols produced through our single-step protocol (where the entire amount of PO was added to the reaction mixture) were found to

have higher levels of unsaturation than those of analogous sucrose-based PEP (Fig. 3). This can be attributed to the additional equivalent of PO required to propoxylate the higher functionalized lactitol ( $f_n = 9$ ) over sucrose ( $f_n = 8$ ). It is known that formation of allylic and isopropenyl ethers (the origins of unsaturation) are dependent upon the initial concentration of PO but independent of the amount of polyether formed.<sup>16</sup> Consequently, the apparent difference between lactitol and sucrose PEP unsaturation could be expected to disappear under continuous feed conditions where the initial PO concentrations would be kept low. In addition, Figure 3 illustrates that for both initiators the amount of vinyl functionality increases with PEP molecular weight, suggesting that the rate of propoxylation is decreasing relative to the rate of unsaturation formation.<sup>17</sup>



**Figure 2** Unsaturation content of lactitol polyols using various catalysts: ( $\blacktriangle$ ) KOH; ( $\circ$ ) triethylamine; ( $\blacksquare$ ) *t*-BuOK.



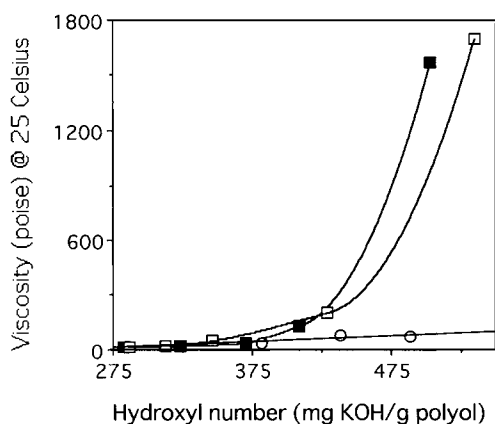
**Figure 3** Unsaturation content of lactitol and sucrose polyols vs. stoichiometric PO/OH ratio: ( $\blacktriangle$ ) lactitol; ( $\blacksquare$ ) sucrose.

### Effect of Extent of Propoxylation on Polyol Viscosity

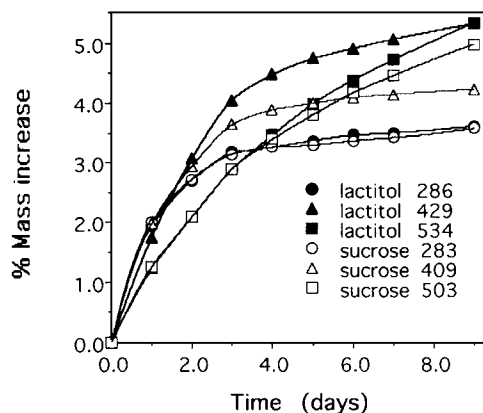
The viscosities of lactitol and sucrose PEP (Fig. 4) are seen to decrease with increasing extent of propoxylation. In contrast to the low viscosity of lactose-based PEP reported by Viswanathan et al.,<sup>6</sup> lactitol appears to give polyols with nearly the same viscosity as that of sucrose PEP of the same hydroxyl number. This supports our hypothesis that removal of the aldehyde function from lactose blocks or significantly slows decomposition reactions which lead to lower-viscosity components. The minimum extent of propoxylation required to yield lactitol PEP of practical viscosity for PURF manufacture (e.g., similar to the voranols) corresponds to a PO/OH ratio of  $\sim 1.7$ .

### Hygroscopicity of the Polyols

The moisture absorption properties of polyols are important during their storage and use in PURF manufacture.<sup>10</sup> During foam formation, water reacts with isocyanates to give urea and biuret linkages and releases carbon dioxide that functions as a blowing agent. The additional crosslinking afforded by moisture can, if excessive, lead to a decrease in PURF dimensional stability.<sup>2</sup> Figure 5 shows the relative moisture absorption (hygroscopicity) of lactitol- and sucrose-based PEP. Polyols exposed to air moisture<sup>18</sup> exhibited rapid initial mass increases which tapered off slowly to equilibrium values. Both PEP showed a trend toward decreasing hygroscopicity with an increased extent of propoxylation (decreased OH#), consistent with previous reports.<sup>19</sup> Hygroscopicity of lactitol PEP appears similar to that of sucrose PEP of the same hydroxyl number.



**Figure 4** Viscosity of polyols as a function of stoichiometric PO/OH ratio: (□) lactitol PEP, (■) sucrose PEP; (○) voranols.



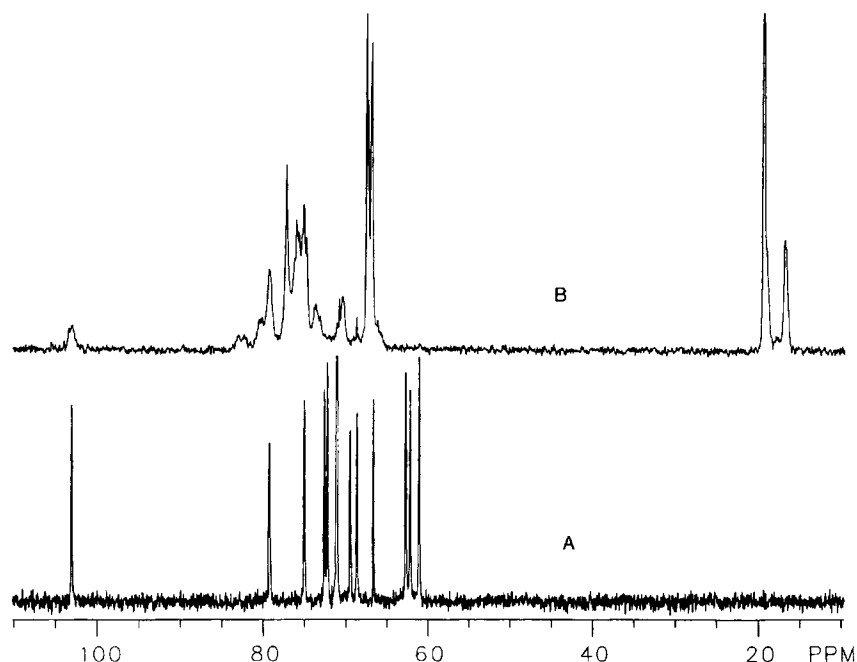
**Figure 5** Hygroscopicity of polyols at 25.7°C and 58.2% relative humidity (nos. indicate OH#).

### Alkaline Stability of Lactitol During Propoxylation

Decomposition of lactitol was considered a possibility under the reaction conditions employed. Lactitol is known to oxidize and/or hydrolyze at high pH and elevated temperatures via formation of 1,2-, 1,4-, and 1,6-anhydrosugars.<sup>20</sup> While infrared spectra indicated no evidence of carboxylic acids or sugar lactones, the <sup>13</sup>C-NMR spectrum of lactitol PEP [Fig. 6(B)] suggests, at least qualitatively, that the disaccharide structure remains intact after propoxylation. The peak at 103.3 ppm (1'-anomeric carbon, galactosyl moiety) can clearly be seen in both starting material and PEP, indicating that the  $\beta(1 \rightarrow 4)$  linkage is not cleaved under the reaction conditions.

### Composition of Lactitol Polyols

Propoxylation of lactitol dihydrate is expected to yield a mixture of products consisting of the distribution of 2-hydroxypropyl adducts as well as oligopropoxyl ethers initiated by water or hydroxide [Scheme (2)]. Indeed, GPC chromatograms (Fig. 7) indicated that lactitol PEP comprised a mixture of high and low molecular weight material. The lactitol-initiated fractions (major peaks) eluted at successively smaller retention volumes with increasing extent of propoxylation, consistent with an increase in molecular size. The lower-weight copolyol fractions, virtually nonexistent in PO/OH = 1, appeared to increase in size and occur in a higher relative percentage as PO/OH increased. Although the lower molecular weight fractions are presumed to be propylene glycol (i.e., water)-initiated oligopropoxyl ethers, whether some propoxylated decomposition products were included remains uncertain. The



**Figure 6** NOE suppressed  $^{13}\text{C}$ -NMR spectra (75 MHz) of (A) lactitol (with dioxane standard at 66.5 ppm) and (B) lactitol-based PEP (PO/OH = 1) in  $\text{D}_2\text{O}$ .

range of retention volumes in which the lower-weight species elute does not preclude this possibility.

### Molecular Weight Distribution

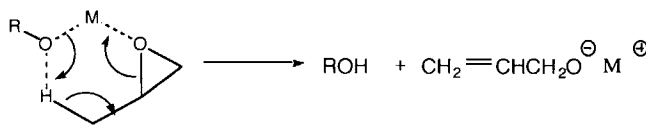
Molecular weight analysis of purified lactitol PEP by GPC indicated that the carbohydrate-initiated fractions were nearly monodisperse. Figure 8 shows there is a narrowing in the molecular weight distribution with increasing extent of propoxylation. The polydispersity indexes ( $M_w/M_n$ ) of the polyols were found to be 1.064, 1.040, and 1.037 for PO/OH = 1, 2, and 3, respectively. Interestingly, these are similar to the values predicted by Flory's Poisson function<sup>21</sup>:

$$M_w/M_n = 1 + \nu/(1 + \nu)^2 \quad (1)$$

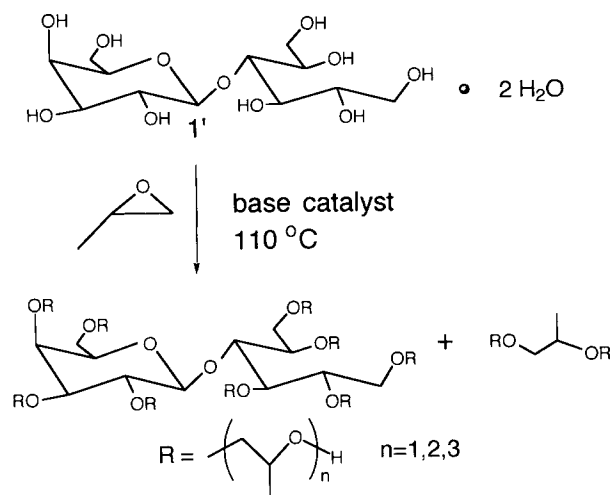
where  $\nu$  is the total number of PO moieties acquired by a molecule of initiator. Figure 9 shows the polydispersity of lactitol PEP and the Poisson polydispersity calculated from eq. (1) plotted against  $\nu$  (the

average maximum number of PO moieties attached to lactitol as determined through  $^1\text{H}$ -NMR). It is surprising that such close correlation exists, considering the requisite assumptions of Flory's treatment, specifically, that all initiator functionality be of equal reactivity throughout the polymerization. The primary hydroxyls of lactitol are expected to be more reactive than are the secondary hydroxyls of its 2-hydroxypropyl adducts. Nonetheless, the nearly monodisperse composition of lactitol PEP is consistent with a rapid proton exchange mechanism known to give narrow molecular weight distributions in polyfunctional initiator systems.<sup>10</sup>

Molecular weights of lactitol PEP estimated from the reaction stoichiometry were found to be lower than the values derived by  $^1\text{H}$ -NMR for the lower homologs, but in close agreement for PO/OH = 3. GPC, on the other hand, gave higher estimates of the molecular weight of all PEP. Table III shows the number-average molecular weights calculated by the above methods. The stoichiometric number-average molecular weight ( $M_n$ ) was calculated from



**Scheme 1.** B-Elimination/activation of propylene oxide



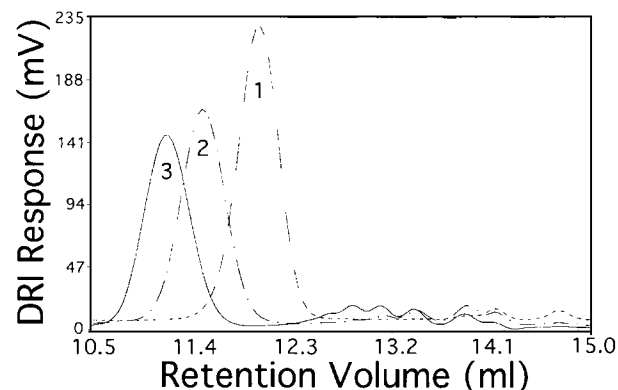
**Scheme 2** Products arising from propoxylation of lactitol dihydrate.

the number of equivalents of PO added to the reaction mixture. Assuming that lactitol and water acquire PO to the same extent,  $M_n$  can be given by

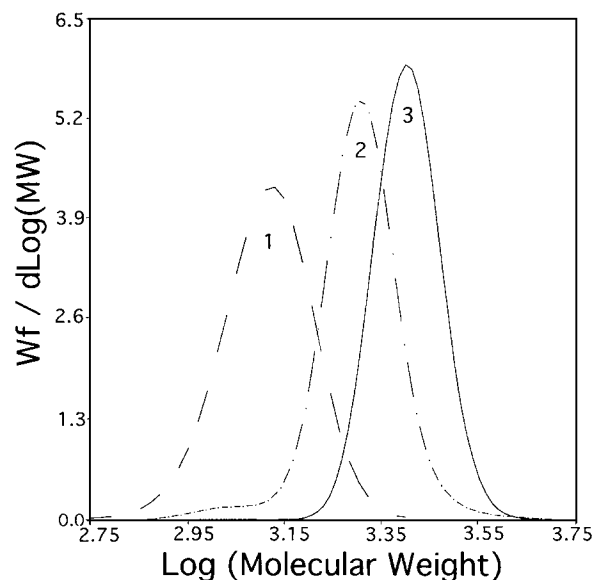
$$M_n = 344.32 + 9(\text{PO}/\text{OH})(58.08) \quad (2)$$

where 344.32 and 58.08 are the formula masses of lactitol and PO, respectively, and (PO/OH) is the stoichiometric ratio of PO to all active hydrogens in the system.

Alternative measurement of  $M_n$  was accomplished through  $^1\text{H-NMR}$  analysis of lactitol-PEP trifluoroacetyl (TFA) derivatives. Lactitol polyols separated from lower-weight copolyols via preparative GPC were reacted with trifluoroacetic anhydride to



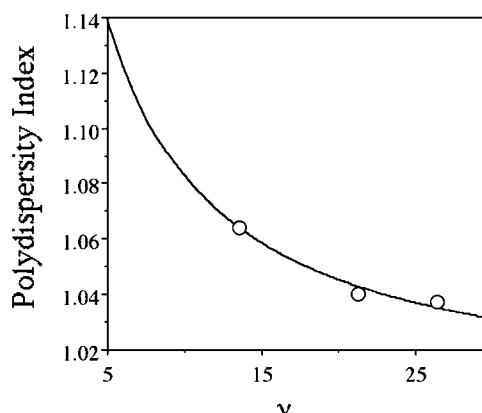
**Figure 7** GPC chromatogram (DRI channel) of lactitol-PEP having stoichiometric PO/OH = 1, 2, 3; 100  $\mu\text{L}$  samples (concn.  $\sim 4$  mg/mL) eluted through two columns in series: 50 + 100  $\text{\AA}$  PLgel with THF mobile phase run at 1 mL/min.



**Figure 8** Molecular weight distribution of purified lactitol PEP (PO/OH = 1, 2, 3).

achieve exhaustive trifluoroacetylation. This strategy effectively deshielded the *exo* 2-propyl ether methyl relative to the *endo* methyl(s) (Fig. 10). Integration of the areas afforded the ratio of internal to external methyls directly proportional to the PO/OH ratio. Assuming that every hydroxyl of lactitol acquires PO moieties according to this ratio, then the molecular weight calculated through eq. (3) represents the maximum  $M_n$ .

The higher initial PO/OH ratios (Table IV) than predicted by the stoichiometry clearly suggests that lactitol is more reactive than is water during the



**Figure 9** Lactitol PEP (O) polydispersity index of found by GPC and Poisson polydispersity (solid line) calculated from eq. (2).  $\nu$  is defined as the no. PO moieties added to lactitol, e.g.,  $9^*(\text{PO}/\text{OH})$ , with the PO/OH ratio from  $^1\text{H-NMR}$ .

**Table III** Values of Lactitol Polyols by Various Methods

PO/OH <sup>a</sup>	$M_n$		
	HPGPC	<sup>1</sup> H-NMR <sup>b</sup>	Stoichiometry <sup>c</sup>
1	1197	1128	866
2	1903	1583	1390
3	2430	1881	1912

<sup>a</sup> Approximate stoichiometric ratio.

<sup>b</sup> Using eq. (3) with PO/OH determined by <sup>1</sup>H-NMR of TFA derivatives.

<sup>c</sup> Derived by eq. (3) using exact stoichiometric PO/OH.

initial stages of propoxylation. This higher reactivity is a reflection of the higher acidity of carbohydrate hydroxyls over water. Accordingly, as the extent of propoxylation increased, the <sup>1</sup>H-NMR-derived PO/OH ratio approached the stoichiometric value as differences in initiator reactivity became negligible, i.e., all initiators became 2-hydroxypropyl adducts.

The difference between  $M_n$  values derived by <sup>1</sup>H-NMR and GPC is anomalous. While the universal calibration method is considered accurate for most polymer molecular weight determinations, deviations have been noted, particularly for lower-weight-polar protic species.<sup>22</sup> <sup>1</sup>H-NMR, on the other hand, has been shown to yield  $M_n$  values with 97% accuracy over a wide range of molecular weights.<sup>23</sup>

Among the significant factors affecting the accuracy of the universal calibration method are flow-rate variation and differences in the solution properties between standards and analytes. While TriSEC software corrects for flow-rate variations, the other factors were not compensated for. Differences in the solution properties of the relatively rodlike polystyrene (DP ca. 5–38) standards are expected to be quite different from those of the spher-

**Table IV** PO/OH Ratios of Lactitol PEP

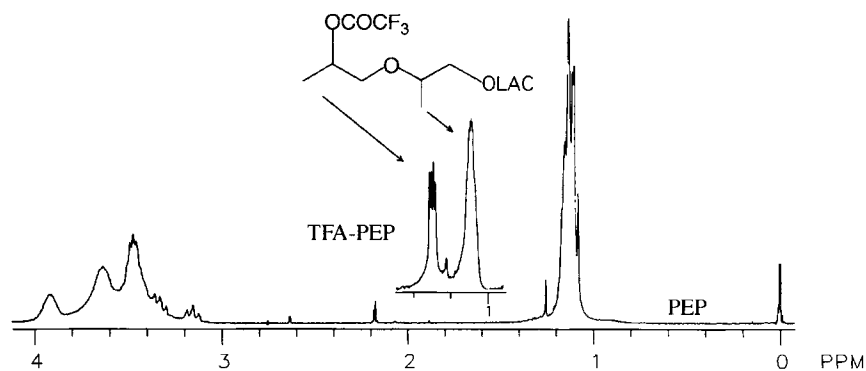
Stoichiometric	<sup>1</sup> H-NMR
0.998	1.5
2.08	2.37
2.98	2.94

ical, hydrophilic PEP. For example, the dependence of hydrodynamic size and viscosity on molecular weight is known to differ between linear and spherical species.<sup>24</sup> Solubility differences can affect accuracy as the universal curve  $\text{Log}(IV \times MW)$  vs.  $RV$  is known to be steeper for better solvated species.<sup>25</sup> In addition, lower retention volumes for especially protic solutes are thought to reflect an enhancement of their molecular volumes through a permanent solvation shell.<sup>26</sup> We are currently investigating the effects of these variables upon the molecular weights calculated by GPC and hope to report a more accurate protocol in a future communication.

### Polyurethane Rigid Foams

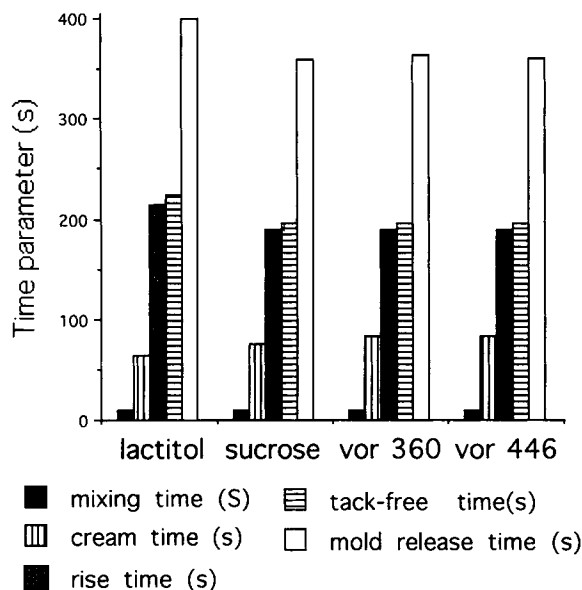
Lactitol, sucrose, and sucrose–glycerin (voranol)-based polyols were observed to have different reactivities toward polymeric isocyanate PAPI. A simple description of the foam formation kinetics can be obtained by observing the macroscopic phenomena of the various time parameters (Fig. 11). Since the length of mixing time, the type and amount of catalyst, blowing agent, and isocyanate index affect the properties of the resulting foams, we choose to fix these parameters in each case.

Lactitol polyethers appear to be more reactive than are sucrose-based PEP and voranols during formation of blown foams. This can be seen by the shorter cream time associated with lactitol–PEP (ca.



**Figure 10** <sup>1</sup>H-NMR spectrum (300 MHz) of lactitol PEP (PO/OH = 2) and methyl region (insert) of the corresponding TFA derivative in  $\text{CDCl}_3$ .





**Figure 11** Time parameters for foam formation using lactitol, sucrose, voranol 360, and voranol 446 PEP with hydroxyl numbers of 420.0, 382.0, 381.8, and 438.22, respectively. Foams were prepared in a  $13 \times 16 \times 16$  cm wooden box coated with wax using formulations given in Table I: Vor = Dow voranol.

65 s) compared to sucrose (76 s) and voranol (85 s). It is interesting that lactitol PEP was more reactive toward PAPI initially, but required a longer tack-free and mold-release time than did the other polyols. A longer rise time and lower PURF apparent core density (Table V) also suggests that lactitol PEP is more reactive toward PAPI; both of these parameters can be linked to PEP reactivity when other variables are held constant. Since all foams were based on the same relative mass of catalyst, blowing agent, surfactant, and isocyanate index, higher functionality should result in a longer rise time and lower PURF core density. The additional hydroxyl content per mol of lactitol PEP over sucrose PEP affords a higher molar heat of reaction with PAPI. This additional enthalpy, when transferred to the blowing agent, provides a longer foam rise time, which, in turn, leads to lower foam density. One practical benefit of the higher reactivity of lactitol PEP could be a reduced requirement for blowing agent to achieve the same PURF density.

The stress/strain curve of PURF is important in determining the potential end uses of the foam.<sup>27</sup> While all foams were seen to exhibit a similar curve (Fig. 12) with compressive strengths (maxima) at approximately 10% deformation, lactitol- and voranol 360-based PURF exhibited slightly lower values, indicating higher friability. Nonetheless, our

**Table V** AACD<sup>a</sup> of Lactitol, Sucrose, and Voranol PEP-based PURF

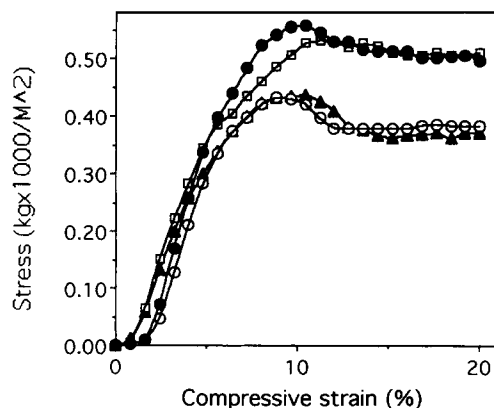
Polyol Type	Apparent Core Density (kg/m <sup>3</sup> )
Lactitol-based	28.9
Sucrose-based	30.8
Voranol 360	33.0
Voranol 446	32.0

<sup>a</sup> AACD = average apparent core densities.

data suggest that lactitol-based PURF prepared by the one-shot process has considerably higher compressive strength than had previously reported lactitol-based PURF prepared according to a two-step prepolymer method.<sup>7</sup> Although the lactitol-based PURF was found to have a lower compressive strength than that of the sucrose-based foam, compressive strength is a function of density. Thus, lactitol-based foam of higher density (e.g., prepared with less blowing agent) would be expected to have compressive strengths comparable to sucrose PURF.

## CONCLUSIONS

Base-catalyzed propoxylation of lactitol under high temperature and pressure affords poly(ether polyol)s (PEP) that compare well with established sucrose-based PURF-suitable PEP. Moreover, lactitol has a processing advantage over sucrose as an initiator by displaying shorter reaction times that are less dependent on particle size. In contrast to



**Figure 12** Compressive strength (in direction of foam rise) of PURF prepared according to formulations given in table I using (▲) lactitol, (□) sucrose, (○) voranol 360, and (■) voranol 446 PEP with hydroxyl numbers of 420.0, 382.0, 381.8, 438.22, respectively.

previous lactose-based PEP, lactitol-based PEP displayed levels of unsaturation, color, and viscosity which lie well within acceptable limits for their use in rigid polyurethane manufacture. Molecular weight analysis of lactitol PEP by GPC showed the lactitol-initiated fraction of the copolyols is nearly monodisperse. While estimation of molecular weights by simple stoichiometric calculation gave lower  $M_n$  values than those estimated by  $^1\text{H-NMR}$ , GPC yielded values significantly higher. Characterization of PURF prepared from lactitol PEP indicates that the foams are of comparable quality to PURF prepared from sucrose and commercially available polyols.

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