

Primary Hydroxyl Content of Soybean Polyols

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Abstract Polyurethanes are obtained by reacting polyols with polyisocyanates. The primary hydroxyl content is a very important characteristic of polyols because it affects their reactivity. Typically primary hydroxyls are approximately threefold more reactive than the secondary hydroxyls when reacting with aromatic isocyanates. This paper presents a simple and convenient kinetic method for determining the primary hydroxyl content in soybean polyols, based on the difference in reactivity of primary and secondary hydroxyls with phenyl isocyanate (PI). The reaction kinetics were studied by following the disappearance of the NCO band at 2260 cm^{-1} with time in the infrared spectra. The reaction of PI with soybean polyols was carried out in a toluene:dimethylformamide (9:1, v/v) mixture. The relative error of the method is in the range of $\pm 5\%$. The method is characterized by simplicity and good reproducibility, and it can be applied to all soybean polyols irrespective of their structure.

Keywords Polyols · Primary hydroxyl ·
Secondary hydroxyl · Soybean oil · Vegetable oil

Introduction

Polyurethanes are obtained by the reaction of a polyol with a polyisocyanate. Polyols from vegetable oils are gaining industrial acceptance, but they bring new challenges in the area of technology and require new analytical techniques.

Various methods can be employed to introduce hydroxyl groups in the triglyceride structure. One of the most common methods for generating hydroxyl groups in the vegetable oil structure is the ring opening of epoxy groups of epoxidized oils with active hydrogen compounds, such as monohydric alcohols, carboxylic acids, water, hydrogen, among others. [1–8]. Unfortunately, this method generates secondary hydroxyl groups that have low reactivity towards isocyanates (Fig. 1).

The reactivity of vegetable oil polyols containing all secondary hydroxyls is lower than that of their petrochemical part, mainly due to the steric hindrances imposed by the dangling chains in fatty acids. However, the reactivity of vegetable oil polyols can be increased by introducing primary hydroxyls using different methods, including hydroformylation [8, 9], ring opening reactions of epoxidized soybean oil with glycols or polyols having primary hydroxyl groups [8, 10], ethoxylation of soybean polyols with secondary hydroxyl groups [11] and transesterification or amidation reactions [8, 12].

With the exception of polyols produced by hydroformylation, which have 100% primary hydroxyl groups, all other methods give a mixture of primary and secondary hydroxyl groups. Determining the primary/secondary hydroxyl content in these polyols is important from both scientific and technological viewpoints. In order to correctly evaluate the primary hydroxyl of soybean polyols, we have applied a kinetic method, based on the difference in reactivity of primary and secondary hydroxyl of soybean polyols with a common reagent, phenyl isocyanate (PI), and evaluated the method precision. The determination of primary hydroxyl content in alcohol mixtures or of polyether polyols by kinetic methods has been described in several papers [13–20]. All of these methods include second order kinetics of the reaction of polyols with acetic

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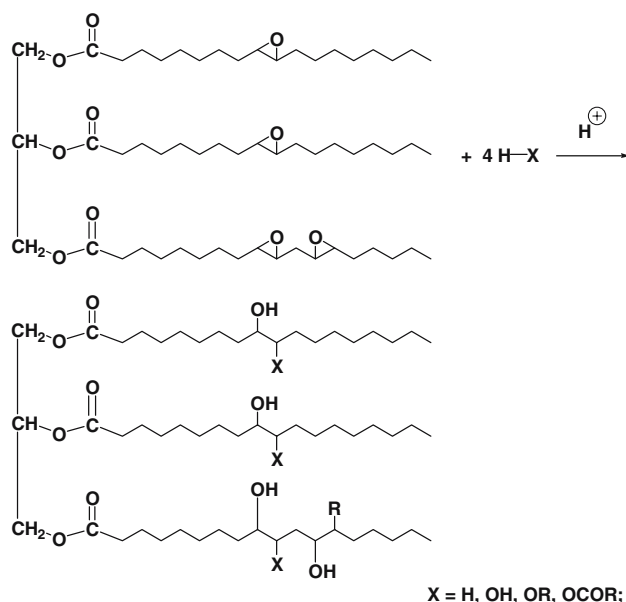


Fig. 1 Formation of soybean polyols with secondary hydroxyl groups by the reaction of epoxydized soybean oil with various hydrogen active compounds

anhydride [13], phthalic anhydride [14] or phenyl isocyanate [15, 16] and pseudo-first order kinetics using a high excess of hydroxyl groups [15] or an excess of phenyl isocyanate or *p*-methyl-phenyl isocyanate [16, 17], or the large difference in reactivity of primary and secondary hydroxyl with triphenylchloromethane [18] or 3-nitrophthalic anhydride [19]. We have used a modified second order kinetics method adapted to soybean polyols described in detail in the literature [15].

Experimental Procedures

Materials

Phenyl isocyanate (99% purity), anhydrous toluene (water content <50 ppm) and anhydrous dimethyl formamide (water content <30 ppm) were purchased from Sigma-Aldrich (St. Louis, MO). DABCO (1,4 diazabicyclo [2,2,2]-octane, also known as triethylenediamine), a solid catalyst, was purchased from Air Products (Allentown, PA). Solutions of DABCO and PI in toluene were prepared in 100-mL volumetric flasks. The reaction mixtures consisting of soybean polyols, PI and DABCO catalyst in toluene–dimethylformamide (DMF) mixture (9:1, v/v) were prepared in 50-mL volumetric flasks. The disappearance of N=C=O groups during the reactions of soybean polyols with PI was followed by measuring the absorbance at 2260 cm^{-1} with time on a Perkin Elmer spectrophotometer (model FTIR-1000; Perkin Elmer–Applied Biosystems, Forster City, CA) using a CaF_2 cell with a 0.1-mm path length.

X-polyol

X-polyol was synthesized by a ring opening reaction of epoxydized soybean oil with methanol in the presence of HBF_4 as catalyst, at $70\text{ }^\circ\text{C}$, as described in detail in the literature [1–7]. All of the hydroxyl groups on the polyol are secondary.

HF-polyol

HF-polyol was obtained by a hydroformylation reaction of soybean oil with syn-gas (CO/H_2) at 1700 p.s.i (11.72 MPa) in the presence of a rhodium carbonyl/triphenylphosphine complex as catalysts. The resulting polyaldehydes were hydrogenated in the presence of Nickel Raney catalyst, as described in by Guo et al. [9]. All of the hydroxyl groups on the polyol are primary.

Ethoxylated soybean polyols

Ethoxylated soybean polyols were obtained by the polyaddition of ethylene oxide to the secondary hydroxyl groups of X-polyol (see Fig. 4) in the presence of HBF_4 as a catalyst under very standard reaction conditions— $35\text{--}45\text{ }^\circ\text{C}$ and 30–40 p.s.i (0.2–0.3 MPa)—as described in the literature [11]. The polyol has both primary and secondary hydroxyl groups as a function of ethylene oxide content.

The water content in all soy-polyols must be a maximum of 0.1%. If the water content is higher than 0.1%, the soy polyol has to be heated for 1–2 h at $100\text{--}110\text{ }^\circ\text{C}$ in a vacuum (10–20 mmHg). Water reacts with isocyanates at a higher rate than secondary hydroxyl [8] and leads to an artificial increase of primary hydroxyl content.

Kinetic measurement of the reaction of soybean polyols with PI

Two solutions were prepared: a solution of PI in toluene and a solution of solid DABCO in toluene.

Preparation of the Solution of PI in Anhydrous Toluene

About 50 mL of dry toluene is added to a 100-mL volumetric flask followed by 10.0 mL (10.95 g) of phenyl isocyanate. The solution is then diluted with anhydrous toluene to 100 mL.

Solution of DABCO Solid in Anhydrous Toluene

About 2.240 g of solid DABCO is added to a 100-mL volumetric flask containing 50 mL of anhydrous toluene. This solution is then diluted with toluene to 100 mL. Each solution is used for approximately ten kinetic

Table 1 Processing of experimental data of reaction kinetics of an ethoxylated soybean polyol with phenyl isocyanate

Number	Time (min)	Absorbance at 2260 cm ⁻¹	$b - x$ (mmol)	x (mmol)	$a - x$ (mmol)	$(b - x)/(a - x)$	$2.303 \times \lg[(b - x)/(a - x)]$
1	0	0.8532	4.9996	0.0003	4.6000	1.0869	0.0833
2	2.25	0.7397	4.3345	0.6654	3.9345	1.1016	0.0968
3	3.58	0.6915	4.0251	0.9479	3.6521	1.1095	0.1039
4	5.16	0.6581	3.8563	1.1436	3.4563	1.1157	0.1220
5	6.42	0.6259	3.6670	1.3323	3.2676	1.1224	0.1154
6	8.22	0.5941	3.4813	1.5186	3.0813	1.1298	0.1220
7	9.42	0.5725	3.3547	1.6452	2.9547	1.1353	0.1269
8	11.12	0.5510	3.2287	1.7712	2.8280	1.1414	0.1322
9	12.42	0.5324	3.1197	1.8802	2.7197	1.1470	0.1372
10	14.47	0.5103	2.9900	2.0097	2.5903	1.1544	0.1436
11	17.42	0.4819	2.8238	2.1761	2.4238	1.1650	0.1527
12	19.12	0.4695	2.7512	2.2487	2.3512	1.1767	0.1627
13	23.42	0.4385	2.5695	2.4304	2.1695	1.1843	0.1692
14	26.12	0.4236	2.4822	2.5177	2.0822	1.1921	0.1757
15	28.17	0.4130	2.4201	2.5798	2.0200	1.1980	0.1806
16	30.15	0.4029	2.3609	2.6390	1.9609	1.2039	0.1856
17	32.44	0.3918	2.2958	2.7041	1.8958	1.2109	0.1914
18	34.42	0.3831	2.2449	2.7550	1.8449	1.2168	0.1962

determinations. In the absence of a catalyst the reaction time required for the analysis is too long by more than 3 h. The use of a conventional tertiary amino catalyst, such as DABCO, considerably shortens the length of an analysis to a maximum duration of 25–35 min.

Procedure

All reactions were carried out in 50-mL volumetric flasks. Polyol (4.6 mmol) was weighed in a 50-mL volumetric flask. The calculation of the quantity of polyol needed in grams was determined using the following formula:

$$\frac{4.6 * 56.1}{\text{OH}\#} = \text{grams of polyol needed}$$

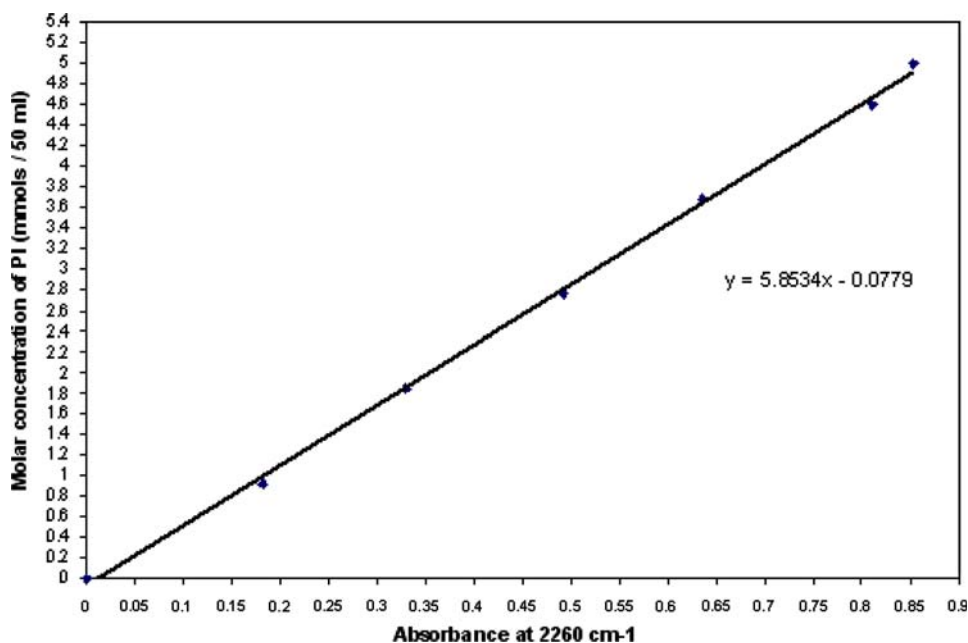
where 4.6 is the desired number of millimoles of hydroxyl groups, 56.1 is the molecular weight of KOH and OH# is the hydroxyl number in milligrams KOH/g.

The polyol was diluted with 25 mL of dry toluene and 5 mL of DMF to which 10 mL of the catalyst solution had been added. The time ($t = 0$) is noted as soon as 5.4 mL (5 mmol) of phenyl isocyanate solution has been added to the flask. The resulting mixture was diluted rapidly with toluene to 50 mL and the flask shaken vigorously for 30–40 s. The reaction mass was injected into a 0.1-mm Fourier transform infrared (FTIR) CaF₂ transmission cell using a 5-mL hypodermic syringe and absorbance recorded. The temperature was maintained constant at 25 °C using a transmission cell heating/cooling jacket (purchased from

Reflex Analytical, Ridgewood, NJ) linked to a thermostat that was especially designated for the reaction kinetics. Spectra are recorded initially every minute (for the first 10 min) and at later stages, at 5-min intervals. The background was recorded with the same cell charged only with the solvent (toluene:DMF, 9:1). The FTIR instrument was set to register the spectra between 2,300 and 2,200 cm⁻¹, and four scans were made. At the concentrations of PI used in the present study ([PI] < 5 mmol/50 mL) the Beer's law is totally respected: a perfect linear relationship between absorbance and molar concentration of the absorbing species (PI) was obtained, with the values of the absorbance units always being lower than 1 (Table 1). This perfect linearity between absorbance and PI concentrations was proven by Willeboordse and Crithchfield [15]. The absorbance can be converted into the molar concentration of PI at any time using the calibration curve presented in Fig. 2.

The primary hydroxyl content is determined graphically from a second order kinetics plot of $\ln[(b - x)/(a - x)]$ as a function of time t , where a is the initial concentration of hydroxyl groups ($a = 4.6$ mmol/50 mL); b is the initial concentration of PI ($b = 5$ mmol/50 mL); x is the concentration of OH groups, in millimoles (equal to the concentration of PI groups) reacted at time t . The procedure for graphical determination of primary hydroxyl is described in detail in the literature [13, 15, 16]. The modifications to the method, as applied here for the first time to soybean polyols, consist in the use of DABCO as the catalyst instead of stannous octoate (stannous octoate

Fig. 2 Calibration curve: the linear dependence of absorbance at 2260 cm^{-1} as a function of phenyl isocyanate (PI) molar concentration. Solvent: toluene:toluene–dimethylformamide (DMF) (9:1, v/v)



loses the catalytic activity with time [15] while the catalytic activity of DABCO does not change with time) and the use of different concentrations of reagents. We experimentally proved that for the same polyol, a DABCO solution stored for 3 months at room temperature, in a volumetric flask, leads to identical kinetic curves as a freshly prepared DABCO solution. The stannous octoate solution, however, loses catalytic activity within several days [15].

Results and Discussion

It is well known that in the non-catalyzed reaction with PI, primary hydroxyl groups are approximately 3.3-fold more reactive than secondary hydroxyl groups and 200-fold more reactive than tertiary hydroxyl groups [8] (Fig. 3).

The content of the primary hydroxyl group of soybean polyols is an important parameter for the selection of an adequate catalyst package in polyurethane formulations. The primary hydroxyl content of petrochemical polyether polyols, which are generally copolymers of propylene

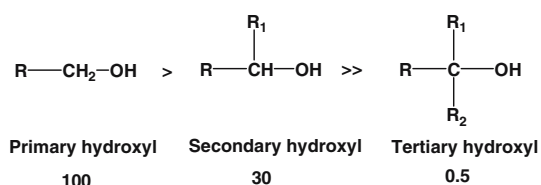


Fig. 3 The relative reactivity of primary, secondary and tertiary hydroxyls toward phenyl isocyanate (non-catalyzed reaction)

oxide and ethylene oxide, is determined by ^{13}C NMR or ^{19}F NMR of derivatized polyols with trifluoroacetic anhydride, as described in ASTM D 4273. Unfortunately, this ASTM method is designed exclusively for determination of the primary hydroxyl content of polyether polyols. To determine the primary hydroxyl content of soybean polyols, we applied a method based on a totally different principle, a kinetic method based on the difference in the reactivity of primary and secondary hydroxyls of soybean polyols with a common reagent, phenyl isocyanate. This kinetic method is a modified second order kinetic method described in detail in the literature [15] and adapted to soybean polyols.

In order to verify the accuracy of the studied second order kinetic method, we used synthetic mixtures of two standard polyols: one polyol with 100% secondary hydroxyl groups obtained by a ring opening of epoxy groups of epoxidized soybean oil with methanol (X-polyol) [1–8], and a second polyol with 100% primary hydroxyl groups obtained by hydroformylation of soybean oil (HF-polyol) [9] (Fig. 4). Six synthetic mixtures of these two soybean polyols with different known content in primary hydroxyls of 10, 20, 30, 40, 50 and 60% were prepared.

Other standard polyols with a well-known content of primary hydroxyl groups were used to verify the method validity: glycerol (primary hydroxyl 66.6%) and 1,2 propylene glycol (primary hydroxyl 50%). The primary hydroxyl content of these synthetic mixtures and standard polyols was determined through the use of the second order kinetic method and comparison with the known values.

An interesting synthetic route to soybean polyols containing primary hydroxyl groups is the ethoxylation

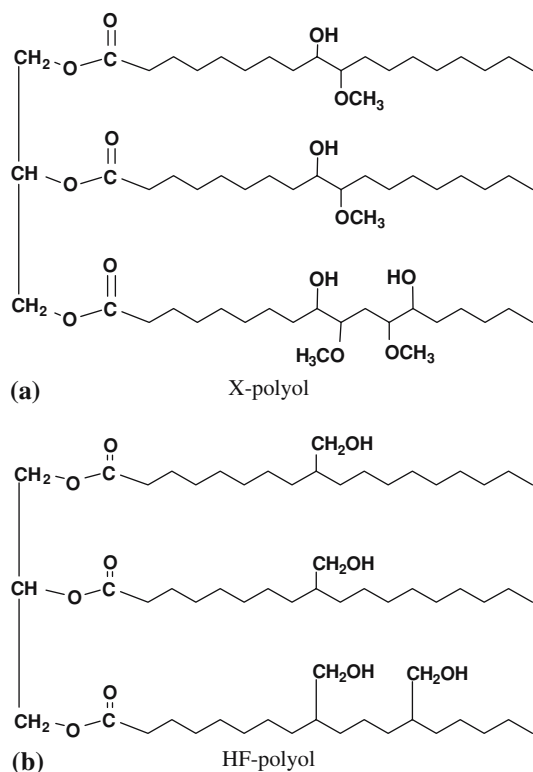


Fig. 4 Schematic representation of a soybean polyol prepared by ring opening of epoxy groups with methanol (X-polyol, **a**) and by hydroformylation (HF-polyol, **b**)

reaction of soybean polyols with secondary hydroxyl groups (Fig. 5). The second order kinetic method was used practically to determine the primary hydroxyl content of some ethoxylated soybean polyols containing 5, 10, 15 and 20% ethylene oxide (EO) units as the terminal block.

To ensure that the studied method could be easily reproduced and applied to other soybean or vegetable oil polyols, the principles of the method and some experimental particularities are briefly presented.

The reactions of hydroxyl groups with isocyanates and with organic anhydrides (acetic anhydride, phthalic anhydride, among others) are typical second order reactions [8, 13, 15]. The reaction of hydroxyl groups with isocyanates has a very simple stoichiometry: one hydroxyl group (compound A) reacts with one isocyanate group (compound B) and generates one urethane group (P = product of reaction). If primary and secondary hydroxyl groups are present together in the reaction mixture, the kinetics become more complex because PI reacts simultaneously with both hydroxyl groups: a higher reaction rate (K_{21}) with primary hydroxyls and a different and lower reaction rate (K_{22}), with the secondary hydroxyls, as illustrated by Eqs. (1) and (2):

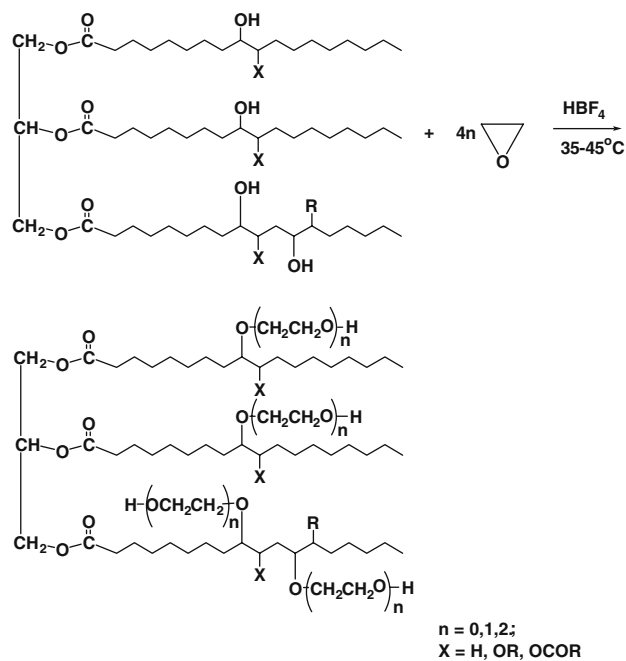
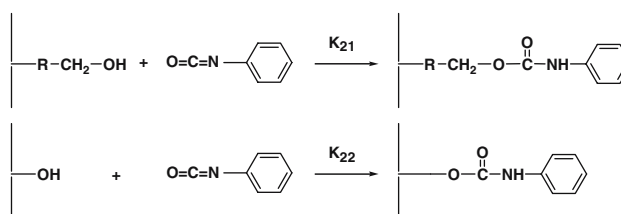
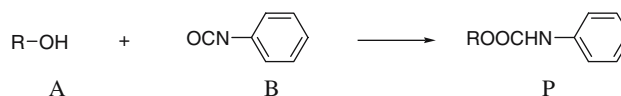


Fig. 5 Formation of soybean polyols with primary and secondary hydroxyl groups by ethylene oxide reactions



The following abbreviations are used throughout this analysis method:

- a initial concentration of hydroxyl groups (mol/L);
- b initial concentration of PI (mol/L);
- x the number of moles of hydroxyl groups reacted at time t = with the number of moles of PI reacted at time t ;
- [A] $a - x$ = concentration of unreacted hydroxyl groups at the moment t (mol/L);
- [B] $b - x$ = concentration of unreacted phenyl isocyanate at the moment t (mol/L);
- t time (min).

The typical kinetic equation characteristic for the second order reactions is presented below:

$$A + B = P$$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = K_2[A][B] = K_2(a-x)(b-x) \quad (3)$$

where K_2 is the second order reaction constant ($L \text{ mol}^{-1} \text{ min}^{-1}$).

Through the separation of variables, integration and the determination of the integration constant we obtained the well-known integrated form of the equation characteristic for the second order kinetics when b is different from a :

$$\ln \frac{(b-x)}{(a-x)} = K_2 t (b-a) + \ln \frac{b}{a} \quad (4)$$

A plot of

$$\ln \frac{(b-x)}{(a-x)}$$

against time t gives a perfectly straight line, with the intersection with ordinate being:

$$\ln \frac{b}{a}.$$

Figure 6 depicts the second order kinetic straight line curves for the reaction of PI with three different polyols in which all hydroxyl groups are identical from a structural point of view: a soy-polyol with 100% secondary hydroxyl groups (X-polyol, Fig. 4a), a hydroformylation polyol with 100% primary hydroxyl groups (HF-polyol, Fig. 4b) and a commercial petrochemical polyether polyol, a homopolymer of propylene oxide with practically 100% secondary hydroxyl groups.

The ratio between the slopes of the kinetic curves of soy-polyols from Fig. 6 is equal to the ratio between the reaction constant of the PI reaction with primary hydroxyl (K_{21}) and with secondary hydroxyl (K_{22}). This ratio is $K_{21}/K_{22} = 8$. The same ratio between the reaction constants of PI reactions with primary hydroxyl of HF-polyol and with the secondary hydroxyl of petrochemical polyol is $K_{21}/K_{22} = 3.3$ (Fig. 6). This result proves that the internal secondary hydroxyl groups in soybean polyols with a higher steric hindrance are less reactive than the secondary hydroxyl groups in petrochemical polyether polyols. The internal secondary hydroxyl in soy-polyols is sterically hindered because it is linked to a carbon atom with two bulky hydrocarbon substituents, each with eight to nine carbon atoms. In the petrochemical polyether polyols, the homopolymers of propylene oxide, the secondary hydroxyl group is less hindered, is a more accessible terminal group and is linked to a carbon atom that has as substituents a polyether chain and the small volume methyl group.

The graphical representation of the second order kinetics of a reaction between PI and a polyol having two different types of hydroxyl groups (e.g. primary and secondary) of

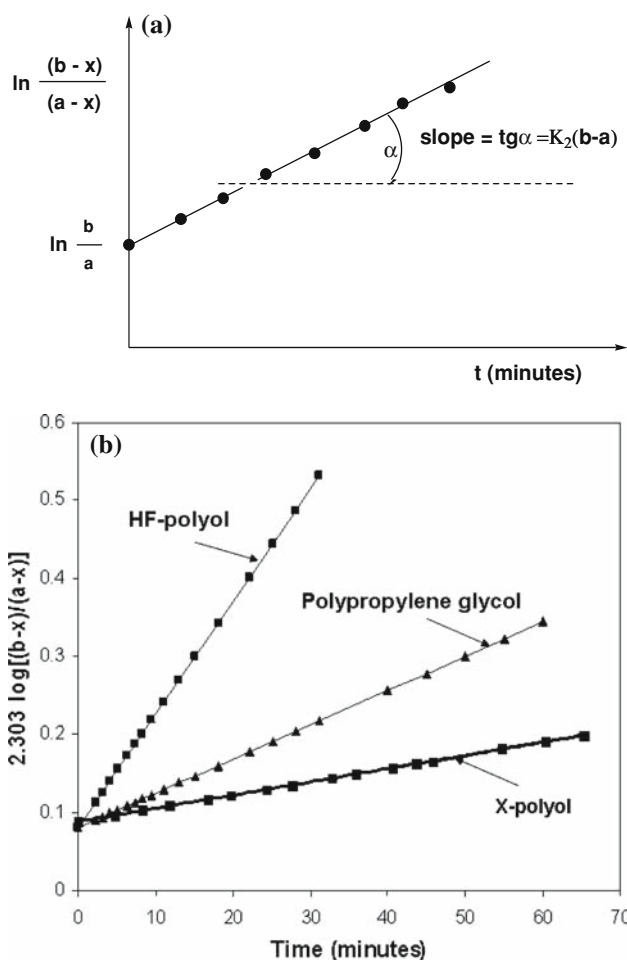


Fig. 6 **a** Second order kinetic curve of the phenyl isocyanate reaction with a polyol with all hydroxyl groups identical from structural point of view. **b** Second order kinetic curves of phenyl the isocyanate reaction with HF-polyol (100% primary hydroxyl content) with X-polyol (100% secondary hydroxyl content) and with a petrochemical polyether homopolymer of propylene oxide (polypropylene glycol of $M = 1000$)

different reactivities consists in two straight lines of two different slopes (Fig. 7). The first straight line, of higher slope, is characteristic of the reaction of the most reactive component (primary hydroxyl) plus some of the less-reactive component (secondary hydroxyl). When the most reactive component (primary hydroxyl group) is totally consumed, the second straight line, the lower slope, is characteristic of the low-reactive component, which remains the secondary hydroxyl group.

The reaction kinetics of soybean polyols with PI was made by following the disappearance in time of the absorbance of the $-N=C=O$ groups in the FTIR spectra at 2260 cm^{-1} . It is very important to make a calibration curve to follow the reaction kinetics: the absorbance of $-NCO$ groups against the molar concentration of PI. Synthetic mixtures were made of PI in toluene/DMF (9:1, v/v) of

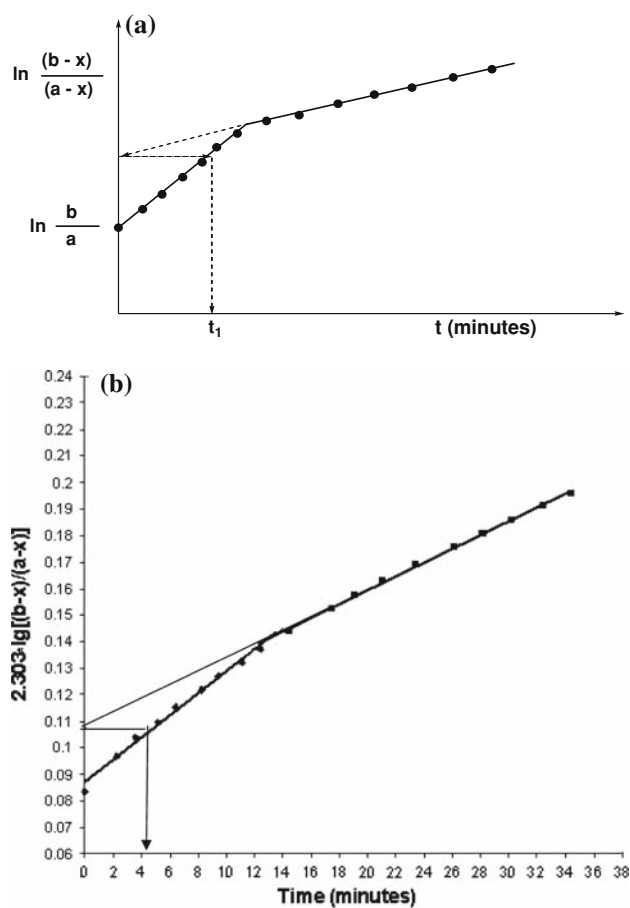


Fig. 7 **a** General graphical representation of the second order kinetics reaction of phenyl isocyanate with a soy-polyol having both primary and secondary hydroxyl groups. **b** Graphical representation of the second order kinetics reaction of phenyl isocyanate with an ethoxylated soy-polyol (15% ethoxylation, 34% primary hydroxyl content)

known molar concentration. By plotting the absorbance against the corresponding molar concentration of PI, we obtained the calibration curve—a perfectly straight line (Fig. 2). During the reaction of PI with soybean polyols the absorbance of -N=C=O groups at 2260 cm^{-1} decreases. With the calibration curve, the absorbance can at any time point be converted into the molar concentration of PI needed for the kinetic calculations.

Based on the experimental data (absorbance at 2260 cm^{-1} against time) a table can be made containing: time, the corresponding absorbance, concentration of unreacted PI ($b - x$), concentration of reacted PI (x), concentration of unreacted hydroxyl groups ($a - x$), the ratio $(b - x)/(a - x)$ and, of course, $\ln[(b - x)/(a - x)]$, as shown in Table 1. All parameters from Table 1 are calculated automatically using EXCEL software. Values $b - x$ are determined easily with the calibration curve. Value x (moles of OH or PI reacting at time t) is obtained by using the relation: $x = b - (b - x)$. Values for $a - x$

are easily determined because a and x are known. The ratios $(b - x)/(a - x)$ and $2.303 \log [(b - x)/(a - x)]$ (in fact $\ln[(b - x)/(a - x)]$) are calculated automatically.

The graphic representation of the second order kinetics by plot $2.303 \log[(b - x)/(a - x)]$ as function of time t is made easily using the data from Table 1. When the structure of soybean polyols are both primary and secondary hydroxyl groups, a graph is obtained with two straight lines, with two slopes (Fig. 7). The primary hydroxyl is determined graphically (Fig. 7a). The straight line representing the reaction of PI with the low-reactive secondary hydroxyl was extrapolated at zero time. From the intersection point a parallel line with the abscissa was drawn until the intersection with the line characteristic to the reaction of PI with the most reactive primary hydroxyl was met. The time corresponding to this intersection point is t_1 . The concentration of primary hydroxyl is the concentration of hydroxyl groups a_1 reacted at time t_1 . The molar percentage of primary hydroxyl groups ($\text{OH}_1\%$) is calculated with the following formula:

$$\text{OH}_1\% = \frac{a_1}{a} \times 100 \quad (5)$$

where a is the initial concentration of hydroxyl groups (at $t = 0$) and a_1 is the concentration of hydroxyl groups reacted at time t_1 . a_1 is determined using the experimental data from Table 1 (a_1 , is the value of x at t_1).

The determined primary hydroxyl content of synthetic mixtures of soybean polyols with a known content of primary hydroxyl and of a number of standard polyols, such as glycerol, propylene glycol and polypropylene glycol of $\text{MW} = 1000$, are given in Table 2. Also shown are some practical results obtained by using the presented kinetic method for determining the primary hydroxyl content of some soybean polyols containing both primary and secondary hydroxyl groups.

Because the mass of the cell and of the spectrophotometer are much higher than the mass of the very small thin layer of material used for kinetics, the exothermal effect of the reaction does not have an important effect. The temperature rises only $0.02\text{ }^\circ\text{C}$ during the 25–30 min period of analysis, which can be considered to be practical in isothermal conditions.

It is very interesting that the acidity of polyols, which has a known decelerating effect, does not affect the determination of the primary hydroxyl content of soy-polyols. For example, a fatty acid (e.g. oleic acid) is added to an ethoxylated soy-polyol with 15% EO and an acid value of 0.2 mg KOH/g to obtain an acidity of 0.5 mg KOH or of 1 mg KOH/g ; the same primary hydroxyl value is obtained—in the range 33–34%—for all the samples. The slope of both straight lines are a little lower as compared with the sample with the lowest acidity, but the

Table 2 Primary hydroxyl content of various polyols determined by second order reaction kinetics of polyols with phenyl isocyanate

Number	Polyol	OH ₁ (%) calculated	OH ₁ (%) determined	Relative error (%)
1	Propylene glycol	50	52.3	4.6
2	Glycerol	66.6	62.0	6.9
3	Hydroformylation polyol	100	100	0
4	Polyol by reaction of ESO with methanol, OH# = 173 mg KOH/g	0		0
5	Synthetic mixture ^a	20	18.9	5.5
6	Synthetic mixture ^a	30	28.8	4.0
7	Synthetic mixture ^a	40	37.9	5.2
8	Synthetic mixture ^a	50	47.8	4.4
9	Synthetic mixture ^a	60	57.9	3.5
10	Polypropylene glycol <i>M</i> = 1000	–	6.0	–
11	Soy polyol by ring opening of ESO with ethylene glycol	–	28.2	–
12	Soybean polyol by ethoxylation of polyol No.4 with			
	(a) 5% EO	–	14.0	–
	(b) 10% EO	–	25.0	–
	(c) 15% EO	–	34.0	–
13	Polyol No.12 c (15% EO) with:			
	AV: 0.2 mg KOH/g	–	34.0	–
	AV: 0.5 mg KOH/g	–	33.2	–
	AV: 1.0 mg KOH/g	–	33.8	–
15	Polyol by reaction of ESO with methanol, with OH# = 56 mg KOH/g, ethoxylated with 15% EO	–	55.8	–

AV acid value, ESO epoxidized soybean oil, EO ethylene oxide

^a Synthetic mixture of a polyol with 100% secondary hydroxyl groups (X-polyol, Fig. 3) hydroformylation polyol with 100% primary hydroxyl groups (HF-polyol, Fig. 3)

change of slopes takes place at the same molar value (the same value for a_1). The same behavior is observed if a substance with an accelerating effect is added; for example, a potassium salt, tin compound or an amine. In this latter case, both slopes are a little higher than those of the non-modified sample, but again the change in the slopes takes place at the same value for a_1 . The successful utilization of DABCO as a catalyst in the studied kinetics is the best example of the effect of a substance with an accelerating effect.

The relative error of determinations is in the range $\pm 5\%$, which is acceptable for the appreciation of the relative reactivity of two soybean polyols. The increase in reactivities of ethoxylated soybean polyols with an increase in EO content can be observed in Table 2. Thus, through the ethoxylation of a soy-polyol without primary hydroxyl (polyol No. 4), with 5, 10 and 15% EO content, the determined primary hydroxyls were 14, 25 and 34%, respectively. In the particular case of a polyol synthesized by the reaction of an epoxidized soybean oil with ethylene glycol (polyol No.11; Table 2), theoretically, the maximum possible primary hydroxyl content to be obtained is 50% because a secondary hydroxyl is formed by the ring

opening of the internal epoxy group with any alcohol. The primary hydroxyl content of this soy-polyol was determined to be around 28.2%, which is considerably lower than 50%. This result can be explained by a part of ethylene glycol with two epoxy groups with the formation of two secondary hydroxyl groups, simultaneous with the extension of soy-polyol chains. The insensitivity of the method to impurities and the simplicity and utilization of conventional FTIR spectrophotometers prove the robustness and flexibility of the method for a correct appreciation of the relative reactivity of soy-polyols toward aromatic isocyanates.

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