Control of Urethane Prepolymerization from Reaction Kinetics and Viscosity*

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Synopsis

A theory of the kinetics of consective second-order reactions has been generalized and used to interpret observations of toluene-2,4-diisocyanate reacting with polyoxypropylene glycol without diluent or catalyst to form a urethane prepolymer. The first reaction in the sequence has a second-order rate constant of 1.2×10^{-7} m^3mole^{-1} sec^{-1} at 303°K with an activation energy of 3.5×10^4 J mole^{-1}. The rate constant of the second reaction appears to be one half of this. Deviations from the theoretical kinetics and an increase in the viscosity of the prepolymer product above 1.9 kg m^{-1} s^{-1} (measured at 313°K) when the temperature of reaction exceeds about 360°K show that above this temperature, undesirable side reactions are important.

INTRODUCTION

On the chemistry leading to polyurethanes, much has been written; see, for example, the review by Entelis and Nesterov[1] or the survey with reference to industrial applications by Johnson.[2] One particularly interesting reaction is the one in which toluene 2,4-diisocyanate and polyoxypropylene glycol form a prepolymer. Because viscosity is an important property of the prepolymer, one must be able to control the reaction so that a product with the desired viscosity is produced and few unwanted side reactions occur. The kinetics of reaction can be readily followed; any deviation from what theory predicts would be evidence for side reactions. Since the reaction occurs in two stages, the kinetics are complex; and although the theory has been developed by Frost and Schwemer,[3] its use has not been emphasized in connection with this system. In the present investigation, we have generalized the theory and used it to interpret our experimental measurements on the uncatalyzed prepolymer reaction at different temperatures. The results, coupled with observations of viscosity, give a clear indication of when the reaction proceeds as desired and when it does not.

The kinetics of isocyanate reactions are well established.[1]   Processes are typically second order, being first order in isocyanate and in the substance containing active hydrogen.   When polyfunctional compounds are present, the reactions can be complicated.   However, with toluene 2,4-diisocyanate, the situation is simplified because the isocyanate in the 2-position is much less reactive than the one in the 4-position.   In a reaction mixture containing twice as many isocyanate groups as active hydrogens, one can assume that only the isocyanate in the 4-position reacts.   Moreover, active hydrogens differ considerably in reactivity; among hydroxyl compounds, a secondary hydroxyl is less reactive than a primary one.   Willeboordse[4] states that the ratio of reaction rates is typically about $1/4$.   Polyoxypropylene glycol, when formed with catalysis by base, contains secondary hydroxyls nearly exclusively, according to Johnson.[2]

We shall suppose that the reaction between it and toluene 2,4-diisocyanate proceeds in two stages.   In the first, one hydroxyl reacts with a 4-isocyanate to yield an intermediate; in the second stage, the remaining hydroxyl in the intermediate reacts with another 4-isocyanate.   The theory of the kinetics in this reaction sequence is presented below.   For the special case where the ratio of reactivities of the two hydroxyls equals $1/2$, the kinetics reduce to those of a single second-order reaction.   Simple second-order theory was used by Wissman, Rand, and Frisch[5] in their study involving various polyether polyols reacting with mixed toluenediisocyanate isomers.   Luckily, in such systems, as our results confirm, the ratio of reactivities is in fact about $1/2$.   One could not expect this usually to be the case, and normally the valid theory, described here, would have to be applied.

THEORETICAL

The reaction of interest belongs to the class described by the consecutive scheme $A + B \rightarrow C + E$ and $A + C \rightarrow D + E$.   Let the second-order rate constants for the first and second reactions be respectively k_1 and k_2.   Here, A is toluene 2,4-diisocyanate, B is polyoxypropylene glycol, and D is the prepolymer (E is nonexistent).   For this system, Frost and Schwemer[3] set up the rate equations, and they solve them in the special case where the initial amounts A_0 and B_0 of A and B are stoichiometrically equivalent, that is, where $A_0 = 2B_0$.   Avoiding this assumption, we suppose that initially $A_0 = \nu B_0$, where ν is arbitrary.   At any time, the amounts A, B and C of the reacting substances must satisfy an equation of material balance $A - 2B - C = A_0 - 2B_0$.   Then C can be eliminated from the rate equations by substituting $C = A - 2B + (2 - \nu)B_0$.   With this substitution and introduction of the dimensionless variables[3] α, β, κ, and τ defined as follows,

$$\alpha = A/A_0 \qquad \beta = B/B_0 \qquad \kappa = k_2/k_1 \qquad \tau = B_0 k_1 t = (A_0 k_1/\nu)t, \quad (1)$$

the rate equations for A and B become

$$d\alpha/d\tau = (2\kappa - 1)\,\alpha\beta - \kappa\nu\alpha^2 + \kappa(\nu - 2)\alpha \qquad d\beta/d\tau = -\nu\alpha\beta \quad (2)$$

where t is the time.   Division yields

$$d\alpha/d\beta = (1 - 2\kappa)/\nu + \kappa\alpha/\beta - \kappa(\nu - 2)/\nu\beta$$

of which the solution is

for $\kappa = {}^1/_2$: $\alpha = 1 - 2/\nu + 2\beta^{1/2}/\nu$

for $\kappa = 1$: $\alpha = 1 - 2/\nu + \beta(2 - \ln \beta)/\nu$

for $\kappa \neq 1$: $\alpha = 1 - 2/\nu + \beta(1 - 2\kappa + \beta^{\kappa-1})/\nu (1 - \kappa)$.

The integration constant is chosen to yield $\alpha = 1$ when $\beta = 1$ (at $t = 0$). Substituting for α in eq. (2) and using the initial condition $\beta = 1$ when $\tau = 0$, one obtains

for[3] $\kappa = {}^1/_2$ and $\nu = 2$: $\tau = 1/\alpha - 1$ $\qquad\qquad\qquad$ (3)

for $\kappa = {}^1/_2$ and $\nu \neq 2$: $\tau = \dfrac{2}{2 - \nu} \ln \left(\dfrac{\nu}{2} + \dfrac{2 - \nu}{2\alpha}\right)$ $\qquad$ (4)

for $\kappa = 1$: $\tau = \dfrac{1}{e^2} \displaystyle\int_2^{2 - \ln\beta} \dfrac{e^u du}{u - (2 - \nu)^{u-2}}$ $\qquad$ (5)

for $\kappa \neq 1$: $\tau = \displaystyle\int_1^\beta \left\{(2 - \nu)u - u^2(1 - 2\kappa + u^{\kappa-1})/(\kappa - 1)\right\}^{-1} du$.   (6)

If $\nu = 2$, the integral in eq. (5) is expressed in terms of the exponential integral.[3]   Equation (6) can be integrated analytically when κ is rational by a complicated procedure similar to the one described earlier.[3]   Today it is faster to integrate numerically with the computer.

In finding k_1 and k_2 from the known A_0 and B_0 and measurements of A or B as functions of time t, by means of these results first α or β is obtained for each time.   Then, if κ is known, one can compute the τ corresponding to each α or β; plotting τ against t yields k_1 from the slope.   The determination of κ which must precede this is less straightforward.   Frost and Schwemer[3] present two methods.   In one, a plot of the experimental α or β against log t is superimposed on the right theoretical curve; in the other, ratios of times required for certain extents of reaction are used with a table to find κ.   To use these methods with the more general theory given here, it would be necessary to prepare curves or a table corresponding to the experimental value of ν, the ones provided earlier[3] being applicable only for $\nu = 2$.

In the usual analytical method, the total concentration of isocyanate groups is determined, which here is equal to $2A + C + 2D$, or $A + A_0$. Denoting the isocyanate concentration relative to its initial value by c, we have

$$c = \alpha + 1.$$ $\qquad\qquad\qquad\qquad\qquad$ (7)

If the measured c drops below unity, evidently isocyanate groups are being removed by side reactions.

An alternative theoretical approach, valid for arbitrary ν, namely, direct integration of the differential equations by computer (digital or analog), is described by Boguth, Repges, and Sernetz[10]; they also analyze the errors involved.

EXPERIMENTAL

Materials

Toluene 2,4-diisocyanate was supplied by du Pont as its brand Hylene T. Polyoxypropylene glycols of nominal molecular weights 400, 1000, and 1200 were given by Jefferson Chemical Canada, the samples being called Jeffox Polypropylene Glycol, Thanol-PPG. According to the literature provided by the manufacturer, both hydroxyls in these materials are secondary. Water is stated to be present to the extent of 0.1%, which is not enough to upset the stoichiometry significantly.[2] Robertson[6] has found that it is not necessary to exclude water with extreme care.

Procedure

Safety precautions were observed because of the dangerously toxic vapors of toluene 2,4-diisocyanate. A reaction flask was fitted with a thermo-couple for reading the temperature, a variable-speed stirrer, a reflux con-denser, and a nitrogen supply. After the flask was purged with nitrogen, a known amount of toluene 2,4-diisocyanate was added, and the temperature was adjusted to its desired value. With stirring, the correct amount of polyoxypropylene glycol was mixed in within 15 sec. Throughout the course of the reaction, the temperature of the mixture was maintained ap-proximately constant, samples being withdrawn at intervals. These were analyzed for isocyanate groups; when the concentration of isocyanate was no longer decreasing, a sample was stored in an airtight container, pre-viously purged with nitrogen, for subsequent viscosity measurements with a Brookfield viscometer.

Analysis of the samples was accomplished by weighing out enough to contain about 1.5 millimole of isocyanate into a glass-stoppered flask, dis-solving it in 25 cm³ dry toluene, adding excess (25.00 cm³) $0.1N$ n-butyl-amine solution, and then, after 15 min of agitation followed by dilution with 100 cm³ anhydrous propanol-2, back-titrating with $0.10N$ hydrochloric acid to a yellow-green endpoint with bromphenol blue. A blank was always subtracted. This method was used by Wissman, Rand, and Frisch.[5]

RESULTS

Kinetics

The relative concentration c of isocyanate decreased at first rapidly and then more slowly, as shown on Figure 1 for experiments with polyoxy-propylene glycol of nominal molecular weight 1000. Using eqs. (3) to (5)

and (7), starting from the relative concentration c, one can calculate the dimensionless time τ necessary for c to attain any value possible theoretically. First, however, it is essential to know κ, the ratio of rate constants. The method of Frost and Schwemer[3] using the ratio of times required for particular extents of reaction yields an average value of $\kappa = 0.5$ from the data at the intermediate temperatures. Although there is an indication that κ increases with rising temperature, it appears that all our data can be analyzed adequately with $\kappa = 0.5$, a value that has the additional advantage of a simple theoretical formula, eq. (3). Our experiments are not well suited to accurate determination of κ; a method for this is reported by Willeboordse.[4]
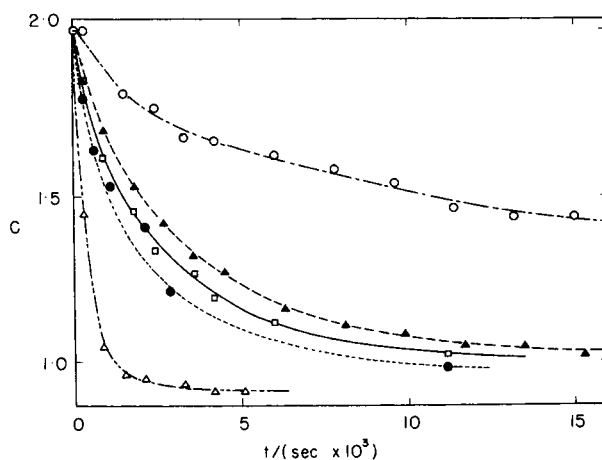

Fig. 1. Measured relative concentration c of toluene 2,4-diisocyanate plotted against time t. Temperatures: 303°K (open circles, dots and dashes), 338°K (filled triangles, dashed line), 353°K (open squares, full line), 373°K (filled circles, dotted line), and 413°K (open triangles, double dots and dashes). Lines are drawn through the experimental points.

When the dimensionless time τ, calculated from the observed c with $\kappa = 0.5$ and eq. (3) is plotted against the actual time t (Fig. 2a), a straight line is obtained initially. We have made analogous plots, calculating τ with $\kappa = 1.0$ and $\kappa = 0.25$ using eqs. (5) and (6); they have a very similar appearance, but fewer points lie on the straight lines. At the later stages of the reaction, side reactions become important, decreasing the relative isocyanate concentration c below its theoretical value. They would include chain extension and reaction of 2-isocyanate. Because the theory predicts that a longer time is necessary, the calculated value of τ is high, and the experimental points on Figure 2a no longer lie on the initial straight line, lying above it instead. The time at which the points begin to deviate from the initial line provides a good indication of when side reactions can no longer be neglected. This has not occurred in the time scale of Figure 2a at $T =$

$303°K$; but at the higher temperatures, side reactions are indeed noticeable, becoming important earlier as the temperature is raised.

By eq. (1), the slopes of the lines in Figure 2a are $A_0 k_1/2$. In these experiments, the initial quantity of toluene 2,4-diisocyanate was 0.1156 kg (0.664 mole); that of polyoxypropylene glycol was 0.3344 kg (one half the equivalent amount, as calculated from the hydroxyl number given by the manufacturer). Assuming additivity of volumes, we find from the specific gravities of the two reactants (given by the manufacturers as 1.22 and 1.01, respectively) that the initial concentration of isocyanate, A_0, is 156 mole m^{-3}. At $T = 303°K$, the rate constant k_1 is thus 1.2×10^{-7} m^3 mole^{-1} sec^{-1}.
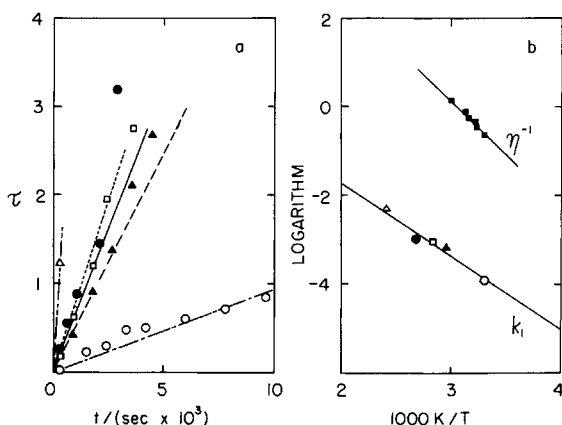

Fig. 2. (a) Dimensionless time parameter plotted against time t according to eq. (3). Symbols have the same meanings as in Fig. 1. (b) Arrhenius plot: abscissa is reciprocal of absolute temperature divided by $1000°K$; lower-line ordinate is $\log_{10} (k_1/\text{l. mole}^{-1}\text{s}^{-1})$; upper-line ordinate is $\log_{10} (\eta^{-1} \text{ kg m}^{-1}\text{s}^{-1})$, where η is the viscosity of prepolymer prepared at $338°K$ from polyoxypropylene glycol of nominal molecular weight 1000.

An Arrhenius plot of $\log_{10} k_1$ against $1/T$ is shown in the lower line on Figure 2b. The slope yields an activation energy E of 3.5×10^4 J mole^{-1}. The corresponding preexponential factor P in the formula $k_1 = Pe^{-E/RT}$ is $P = 0.10$ m^{3}mole^{-1}s^{-1}. Here, the gas constant $R = 8.31$ J $°K^{-1}$ mole^{-1}. The value of k_1 at $T = 323°K$ is 2.8×10^{-7}m^{3}mole^{-1}s^{-1}, which may be compared with 1.0×10^{-7} m^{3}mole^{-1}s^{-1} found by Wissman, Rand, and Frisch[5] for the uncatalyzed reaction of a mixture of 78.9% toluene 2,4- and 21.1% toluene 2,6-diisocyanate with polyoxypropylene glycol (MW = 980) at $323°K$. They do not report the activation energy for the uncatalyzed reaction, but Tanaka, Yokoyama, and Iwasawa[7] obtained $E = 3.3 \times 10^4$J mole^{-1} for benzene 1,4-diisocyanate reacting with polyoxypropylene glycol in chlorobenzene solution. Hartley, Cross, and Lord[8] found $E = 3.5 \times 10^4$J mole^{-1} in a prepolymer flexible-foam system consisting of a polyether and toluene diisocyanate.

Viscosity

Also measured was the viscosity of the prepolymers resulting from each of the experiments of Figure 1 and of the prepolymers prepared at 338°K with polyoxypropylene glycols of nominal molecular weight 400 and 1200. From a plot of the viscosity η, measured at 313°K, against the temperature of the reaction used to prepare the prepolymer (Fig. 3), one sees that reaction temperature has little influence below about 360°K, but above this temperature the viscosity rises very sharply. How the viscosity of a single prepolymer sample depends on the temperature of measurement can be represented adequately by an Arrhenius equation $\eta^{-1} = Pe^{-E/RT}$, as one sees from the upper line on Figure 2b. Over this narrow temperature range, it is not necessary to use the type of plot reviewed by Fox, Gratch, and
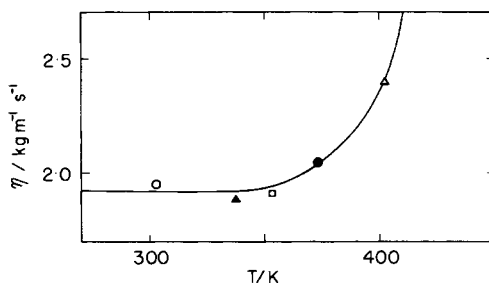

Fig. 3. Viscosity measured at 313°K of prepolymers prepared from polyoxypropylene glycol of nominal molecular weight 1000, plotted against the temperature of the reaction.

Loshaek[9] in which the logarithm of the viscosity is plotted against a higher power of the reciprocal temperature. The activation energy E is 4.7×10^4 J mole^{-1}. Similar plots for the prepolymers from glycols with molecular weights 1200 and 400 (not shown) yielded the same activation energy. However, at a given temperature, the viscosity decreased as molecular weight increased, instead of increasing as expected. This may be because of increased flow resistance in the material of lower molecular weight where a higher proportion of the bonds are in the benzene ring and in urethane links; or the course of the reaction with the lower glycol may be different from that assumed, leading to products of higher average molecular weight.

CONCLUSIONS

A convenient description of the theory describing the kinetics of consecutive second-order reactions has been given. This theory is applicable to the reactions between toluene 2,4-diisocyanate and polyoxypropylene glycol in which a urethane prepolymer forms. For the first reaction in the sequence, the values of the rate constant and activation energy are comparable to those found by other workers with similar systems. The second re-

action appears to proceed with one half the rate constant of the first. Deviations from the theoretical kinetics and a marked increase in the viscosity of the prepolymer when the reaction temperature exceeds 360°K show that to avoid side reactions, the process should not be carried out above this temperature. The experimental methods utilized here are simple and can be applied in small laboratories without costly equipment.

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