The main conclusion from this work is that the porous layer model, combined with the Scheutjens–Fleer adsorption theory is able to predict the variation of hydrodynamic layer thickness of adsorbed polymer layers with coverage and with molecular weight quite well. The dominant contribution to this thickness comes from long tails, which extend far into the solution.

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Properties of Partially Cured Networks. 1. Curing Kinetics of a Model Network

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ABSTRACT: Model networks based on α,ω-dihydroxypoly(propylene oxides) and tris(4-isocyanatophenyl) thiophosphate were prepared. The curing kinetics were followed up to 97% conversion by measuring the change in the infrared absorption intensity of the isocyanate stretching band at 2200–2300 cm^{-1}. The overall reaction kinetics were found to be second order and are described well by a scheme consisting of competitive consecutive order reactions up to an extent of reaction of about 85% (the gel point). The observed increase in reaction rate at conversions greater than 85% is attributed to an increase in intramolecular reactions.

In the past few years dynamic mechanical tests have been widely used to monitor the changes in viscoelastic response during network formation.[1-10] The aim of such measurements is to determine the time dependence of the state of cure and the curing mechanisms of thermosets and finally to understand network formation and properties on the molecular level. Such knowledge can then lead to optimization of curing processes.

Properties of partially cured networks can be obtained by two principally different methods. The first involves quenching of the cross-link reaction by cooling or by addition of fast-reacting monofunctional agents at different reaction times to produce samples at various states of cure.[8] Disadvantages of adding monofunctional reactants are that this does not work in the postgel region of fast-curing thermosets and that the system is altered by the treatment. Some parameters, like sol content, however, can only be measured in this way.

The other method relies on measurement of properties while the cross-like reaction continues. This method requires either that the property changes caused by the ongoing cure are small in the time scale of the measurement or that they are taken into account.[6] Furthermore, to relate the measured properties to the state of cure the curing kinetics have to be known.

In this paper we describe synthesis and kinetics of a system that is well suited for investigation of properties of partially cured networks.

System

Many of the investigations of curing processes have been conducted with chemically very complex systems[1-7] so that the data obtained are difficult to explain on a molecular basis. Since the study of model networks has been successful in the interpretation of structural dependencies of fully cured networks,[11] the application of the same concept to investigate properties of partially cured networks seems reasonable.[8,10] A model network-forming system suitable for the intended studies has to fulfill the following criteria: the network formation should be noncatalytic and slow at room temperature and form no byproducts. Furthermore, there should be a convenient analytical technique to elucidate the kinetics of the curing reaction. Finally, the glass transition of the system during the cure should always be below the curing temperature. All these requirements are satisfied by a system consisting of α,ω-dihydroxypoly(propylene oxide) and tris(4-isocyanatophenyl) thiophosphate. Similar systems have been used by Andrady[12] and with a different trisisocyanate by Sung and Mark.[13]

Materials

α,ω-Dihydroxypoly(propylene oxides) of nominal molecular weight 1000 and 3000 were obtained from Aldrich Chemical Co. The molecular weights obtained by vapor pressure osmometry are 1170 and 2820. Analysis for OH groups show that the PPO's have a functionality of approximately 2.0 ± 4%. This is in agreement with the results of Sung and Mark.[13] The fraction of

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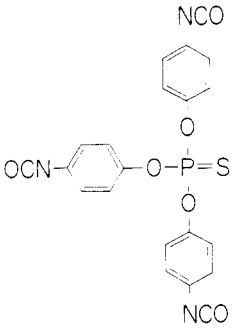

Figure 1. Tris(4-isocyanatophenyl) thiophosphate.

primary hydroxyl groups is assumed to be 2.5% (PPO 1000) and 9.5% (PPO 3000).[14]

Following Vakhtina et al.,[50] the content of monofunctional material in PPO 1000 and 3000 was analyzed by thin-layer chromatography (liquid phase: ethyl acetate–1% *sec*-butyl alcohol). No traceable amounts of monofunctional material were found in PPO 1000, but PPO 3000 contains about 5% monofunctional PPO. This is confirmed by GPC measurements with a Waters GPC-II (columns: 500, 10^3, 10^4, and 10^5 Å; Ultrastyragel; mobile phase: THF at 25 °C, 1150 psi, and 1.00 mL (min)), which give the molecular weight distribution for PPO 1000 (M_w/M_n = 1.05) and for the difunctional part of PPO 3000 (M_w/M_n = 1.09).

Prior to use, the PPO is mixed with benzene (pa), which is then distilled off to remove water traces azeotropically.[15] The excess benzene is removed under vacuum at temperatures up to 60 °C.

Tris(4-isocyanatophenyl) thiophosphate ("triisocyanate") (Figure 1) is obtained as the methylene chloride solution (Desmodur RF (Mobay Corp.)). The yellow solution is concentrated to about one-third of the volume and cooled to 4 °C for 1–2 days during which the triisocyanate starts to crystallize from the solution. The crystallization is completed at −18 °C for another 1–2 days. The yellow solution is removed, and the remaining white crystals are dissolved in dry benzene and finally freeze-dried to obtain a white powder (mp 84.1–84.8 °C).

To obtain the curing mixture, equimolar amounts of triisocyanate and PPO are mixed under vacuum, forming a white slurry, which is then heated to 90 °C for 1–4 min. The resulting clear colorless solution is immediately cooled in an ice bath and subjected to the measurements. All experiments are accomplished under an inert-gas atmosphere. The completely cured products are colorless or slightly yellow and transparent.

Nomenclature. α,ω-Dihydroxypoly(propylene oxide) is abbreviated as PPO; the number following the acronym indicates the nominal number-average molecular weight. Triisocyanate refers to tris(4-isocyanatophenyl) thiophosphate.

Kinetics

Kinetics of uncatalyzed reactions of isocyanates with alcohols have been widely investigated.[15-18] The reaction is considered to be described by

$$\mathrm{RNCO} + \mathrm{B}_j \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{Y}$$

$$\mathrm{Y} + \mathrm{R'OH} \xrightarrow{k} \text{urethane} + \mathrm{B}_j$$

where B_j can be any substrate with a free electron pair, e.g., alcohol, urethane, or solvent. For aromatic isocyanates $k_{+1}, k_{-1} \gg k$ so that the kinetics are governed by the rate constant k. The rate expression for the kinetics of the urethane formation is then given by

$$\mathrm{d[NCO]}/dt = -\sum_j k_j[\mathrm{NCO}][\mathrm{ROH}][\mathrm{B}_j] \qquad (1)$$

The brackets denote concentration of isocyante (NCO), alcohol (ROH), and complex-forming substrate (B_j). We assume that in bulk PPO the activated complex is formed solely with the PPO ether groups.[48] $[B_j]$ is therefore constant and the overall kinetics for the bulk phase urethane formation are fit to a rate expression of second order.[22-25]

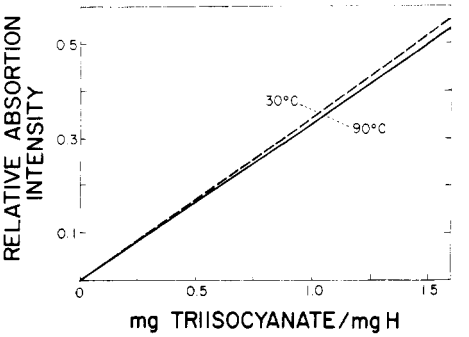

Figure 2. Correlation between the absorption ratio NCO:CH and (milligrams of triisocyanate):(milligrams of aliphatic H) measured for mixtures fo triisocyanate with phenyl isocyanate end-capped PPO 3000 at 30 and 90 °C.

Assuming that the change in NCO concentration with reaction time is due only to the reaction between isocyanate and alcohol, the reaction kinetics can be investigated by measuring the change in the infrared absorption intensity of the isocyanate N=C stretch band at 2200–2300 cm^{-1}.[24,26] The C–H absorption intensity at 2650–3030 cm^{-1} is used as an internal standard[27,24] to adjust for thickness changes of the samples.

The absorption of the N=C band follows Beer's law[17,18,24,28] and is free of interference in urethane-forming systems;[24] the extinction coefficient depends on the dielectric constant of the medium.[17] Correlation functions for absorption intensity at 2120–2400 cm^{-1} vs. triisocyanate NCO concentration in PPO 3000 end capped with phenylisocyanate are given at two temperatures (Figure 2). The observed temperature dependence is consistent but small compared to the error range of the measurements. The NCO concentration is given in milligrams of triisocyanate per milligram of aliphatic hydrogen (H), allowing the use of the same correlation independent of the actual molecular weight of the PPO used in the respective mixture.

Absorption data in this paper are presented in terms of the extent of reaction p calculated by[24]

$$p = ([\mathrm{I}]_0 - [\mathrm{I}])/[\mathrm{I}]_0 \qquad (2)$$

The brackets denote concentrations of isocyanate (I) at reaction time $t = 0$ (index 0) and $t = t$ (no index). $1/(1 - p)$ is plotted vs. time, which for simple second-order reactions results in a straight line of the form[24]

$$1/(1-p) = [\mathrm{I}]_0/[\mathrm{I}] = [\mathrm{I}]_0 kt + 1 \qquad (3)$$

with k being the rate constant. This representation allows comparison of results obtained from various absorption bands. The dependence of the extent of reaction p on the carboxy and the secondary amide group concentration, respectively, is given by

$$p = \frac{[\mathrm{CO}]}{[\mathrm{CO}]_\infty} = \frac{[\mathrm{NH}]}{[\mathrm{NH}]_\infty} \qquad (4)$$

the index ∞ indicating the respective concentrations at complete reaction. These bands are less sensitive than the NCO band and not free of interference, e.g., hydrogen bonding. The kinetics obtained from them are therefore less accurate. However, monitoring of these bands allows detection of side reactions that consume NCO but do not lead to urethane formation. Urea formation was not detectable by the presence of the amide I band at 1660 cm^{-1} [49] in any of the spectra.

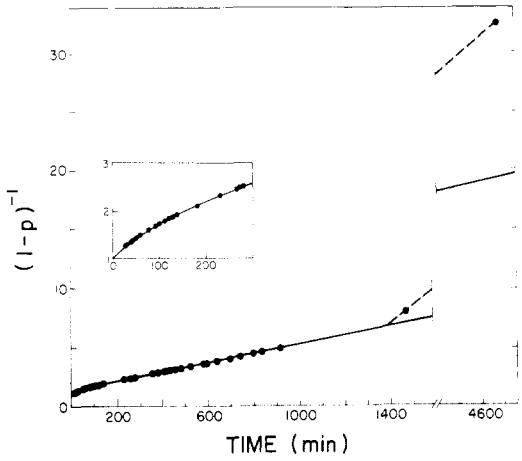

Figure 3. $1/(1 - p)$ vs. time measured by NCO absorption intensity for cure of PPO 1000 with triisocyanate at 30 °C ($[NCO]_0$ = 1.526 mmol g^{-1}; solid line calculated with eq 7). Inset shows the first 300 min enlarged.

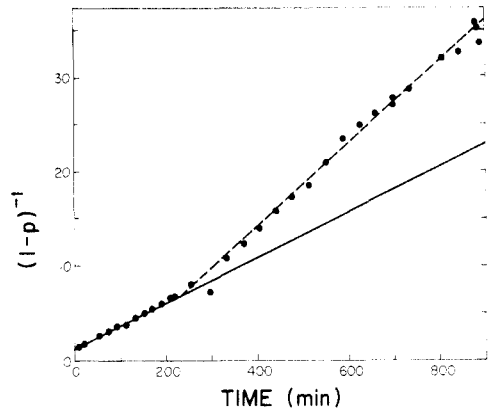

Figure 4. $1/(1 - p)$ vs. time measured by NCO absorption intensity for cure of PPO 3000 with triisocyanate at 90 °C ($[NCO]_0$ = 0.604 mmol g^{-1}; solid line calculated with eq 7).

FTIR Experimental Method

Infrared spectra were obtained on a Nicolet 7199 Fourier transform infrared spectrometer. Spectra of the kinetic runs were taken with a software-controlled data collection routine. All spectra were run at 2-cm^{-1} resolution and were signal averaged for 100 scans.

To follow the kinetics, a drop of the clear PPO–triisocyanate mixture was placed between thin preheated KBr plates, which were then mounted in a preheated Harrick variable-temperature liquid cell pressing the sample to a thickness of 12 μm. The temperature was measured at the aluminum frame of the cell and was kept constant to within ±0.5 °C.

Results and Discussion

Kinetics in the Pregel Region. Figures 3 and 4 show plots of $1/(1 - p)$ vs. time obtained by FTIR measurement of the isocyanate absorption for reaction of triisocyanate with PPO 1000 at 30 °C and with PPO 3000 at 90 °C, respectively. It is obvious that the reaction cannot be described by simple second-order kinetics. The reaction scheme is given by

$$(OCN(1,4\text{-}C_6H_4)O)_3PS \xrightarrow[+ROH]{k_1}$$

$$(OCN(1,4\text{-}C_6H_4)O)_2(ROOCNH(1,4\text{-}C_6H_4)O)PS \xrightarrow[+ROH]{k_2}$$

$$(OCN(1,4\text{-}C_6H_4)O)\,(ROOCNH(1,4\text{-}C_6H_4)O)_2PS \xrightarrow[ROH]{k_3}$$

$$(ROOCNH(1,4\text{-}C_6H_4)O)_3PS \quad (5)$$

Table I
Reaction Constants[a] and Activation Energies

temp, °C	k_1	k_2	k'	k''	$k'' - k_2$
30	7.50	2.50	2.50	5.34	2.84
90	90.0	40.0	40.2	72.8	28.6
E, kJ mol^{-1}	38	42	42	40	35

[a] In g mol^{-1} min^{-1}.

with ROH = alcohol and $(1,4\text{-}C_6H_4)$ = 1,4-substituted phenyl or

$$A_3 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_1 \xrightarrow{k_3} A_0 \quad (6)$$

where A denotes the different states of the cross-linker and indices 0–3 indicate the number of unreacted NCO groups. k_1 to k_3 are the rate constants for the respective reactions. If each urethane group is formed by the same second-order mechanism, then the observed kinetics should be describable as a competitive consecutive irreversible second-order reaction.[29] As studies of the glass transition change with conversion show,[45] the considered curing reaction is diffusion controlled after a short initial period. This is further supported by the fact that the apparent activation energy of the diffusion coefficient of PPO (M_n = 10 000) in a matrix of PPO (M_n = 38 000 and M_w = 60 000) is of the same order of magnitude (E_a = 43.9 kJ/mol)[46] as the one obtained here (E_a = 42 kJ/mol; see below). If we assume that the reaction becomes diffusion controlled for all isocyanate groups bound by a urethane group to a PPO molecule, then k_2 and k_3 should be equivalent. For the case that [ROH] = [NCO], the decrease in isocyanate concentration in the system should be described by (see Appendix)

$$d[NCO]/dt = 3(k_2 - k_1)[ROH][A_3] - k_2[ROH]^2 \quad (7)$$

The solid lines in Figures 3 and 4 describe the data very well and are calculated with eq 7 with k_1 = 7.5 g mol^{-1} $min,^{-1}$ k_2 = 2.5 g mol^{-1} min^{-1}, and $[ROH]_0 = 1.526 \times 10^{-3}$ mol g^{-1} of mixture at 30 °C and k_1 = 90 g mol^{-1} min^{-1}, k_2 = 40 g mol^{-1} min^{-1}, and $[ROH]_0 = 6.042 \times 10^{-4}$ mol g^{-1} of mixture of 90 °C. The integration of eq 7 was obtained numerically. Rate constants and activation energies are summarized in Table I, showing that the activation energy for k_2 is higher than for k_1.

Kinetics in the Postgel Region. With the model of competitive consecutive second-order reaction, the kinetics of the investigated system are described well up to an extent of reaction of 85.5% (30 °C) and 86.4% (90 °C). Above that conversion the overall rate constant changes from k' = 2.50 g mol^{-1} min^{-1} (90 °C). k' and k'' are the overall rate constants before and after the rate increase. They are obtained by dividing the slopes in the second order plots (Figures 3 and 4) by the concentration of NCO groups at time t = 0 (1.5261 mmol g^{-1} of mixture for PPO 1000 and 0.6042 mmol g^{-1} of mixture for PPO 3000) according to eq 3. k' equals k_2 as well as the first term on the right-hand side of eq 7 becomes negligible. The overall reaction mechanism after the rate increase is still of second order. As the results in Table I show, the activation energy obtained from k'' is smaller than from k'.

The consecutive second-order model with $k_3 > k_2 < k_1$ was used to try to explain the increase in reaction velocity. No set of parameters could be found to fit the data, however.

Changes in apparent reaction rate for reactions of isocyanates with alcohols are frequently observed. Anzuino et al.[16] attribute a slight velocity increase for the reaction of MDI with α,ω-dihydroxypoly(oxytetramethylene) to allophanate formation (Figure 5). This side reaction is

Figure 5. Allophanate formation showing that the NH concentration remains unchanged.

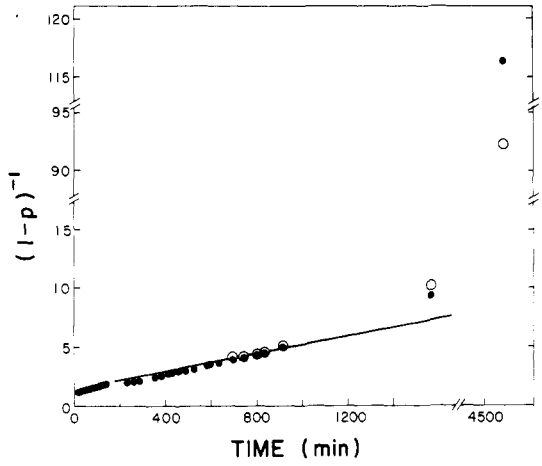

Figure 6. $1/(1-p)$ vs. time measured by NH absorption peak lights for cure of PPO 1000 with triisocyanate at 30 °C (solid line calculated with eq 7).

significant for most systems only at elevated temperatures (>100 °C),[22,35,36] but may be important even at 40 °C.[18] The NH group concentration is not affected by allophanate formation. Following the change in NH group absorption with time and comparing it to the kinetics obtained by the NCO group absorption should therefore show if allophanate formation plays a role. The plot of $1/(1-p)$ for the NH absorption vs. time at 30 °C measured by peak heights at 3300 cm^{-1} (Figure 6) shows only minor differences when compared to Figure 3. They are attributed to the low accuracy for the measurements of the NH band in the presence of hydroxyl groups. Allophanate formation therefore is considered insignificant in this system.

Autocatalysis is another factor influencing the kinetics of isocyanate reactions[15,19] but is not observed in reactions of aromatic urethanes in polar media.[17] Furthermore, model calculations[37] show that this model is not able to describe the observed change in reaction velocity.

At moderate extents of reaction an increase in reaction rate was also observed for the reaction of HDI with a specific alcohol, 2-ethyl-1,3-hexanediol, but not with other alcohols.[18] The factors leading to rate increases in this case are not satisfactorily explained. However, they may be of some other origin than in the case of network formation where rate increases are observed in systems differing in isocyanate and alcohol component.

Changes in overall reaction rate due to gel formation have been observed in polyurethane, polyester, and epoxy systems. In many cases the reaction is found to slow down[10,30-32] or even to stop completely.[32,33] For a system of polymethylene–poly(phenyl isocyanate) (f = 2.7) and a polyether–polyol based on sorbitol (f = 4.8), Marciano et al.[25] show that the dibutyltin dilaurate catalyzed reaction slows down considerably after the gel point but that the uncatalyzed reaction is not affected. Their adiabatic temperature rise data even suggest that at very high extents of reaction the reaction velocity increases. Mussati[8,34] reports an increase in reaction velocity for a system of a diol, MDI, and an ϵ-caprolactone-based triol. No explanation is given.

Vilesova et al.[38] report that the overall second-order reaction rate for the system PPO–triol and TDI is not affected by the gel point and does not depend on the conversion. Due to the differing reactivity of the NCO groups in TDI[39] a decrease in the reaction velocity with time would be expected.[17] The unchanged reaction rate, therefore, seems to indicate an actual increase in reaction rate.

One of the most successful theories in describing pre- and postgel kinetics is Gordon and Scantlebury's spanning-tree approximation for f-functional polycondensation processes incorporating cyclization reactions.[40-42] The model allows one to consider first-shell substitution effects as well as competition between inter- and intramolecular reactions. Unfortunately, the mathematical calculation of the rate expressions is very complex and therefore not attempted is this work. Besides, the description of the investigated reaction by the competitive consecutive second-order model is successful up to high conversion. Obviously the curing kinetics are little influenced by ring formation in the pregel region. This is to be expected[41-44] because intramolecular reaction is generally not important until there are sufficient amounts of molecules with extremely large molecular weight ($M_w \rightarrow \infty$). Only with the rapid increase in the numbers of functional groups per molecule near the gel point does the intramolecular reaction become significant. By the intramolecular reaction the movement of neighboring functional groups away from each other is reduced, thus promoting further intramolecular reaction.[43,47] Eventually the segmental mobility becomes reduced below the level that intramolecular cross-linking itself requires, and a more or less marked decrease in overall reaction rate is observed. Of course, if the segmental mobility is little influenced by the cross-link density—and that seems to be the case for PPO–urethane networks[12,45]—an increase of the amount of intramolecular reaction should be observed. At this time we can think of no better explanation for this relative sudden increase in overall reaction velocity above 80% (Figures 3 and 4) than to attribute it to an increase in the portion of intramolecular reaction. To substantiate this theory, further experimental data will be necessary.

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Appendix

Consider a competitive, consecutive reaction of a molecule, A_3, with three functional groups A and equivalent amounts of reactant B:

$$A_3 + 3B \xrightarrow{k_1} A_2 + 2B \xrightarrow{k_2} A_1 + B \xrightarrow{k_1} A_0 \quad (8)$$

The indices 3 to 0 denote the number of unreacted groups A. The rate equation for [A] or [B] is then given by

$$d[A]/dt = -3k_1[A_3][B] - 2k_2[A_2][B] - k_3[A_1][B] \quad (9)$$

If $k_2 = k_3$

$$d[A]/dt = -3k_1[A_3][B] - k_2(2[A_2] + [A_1])[B] \quad (10)$$

with

$$[A_3]_0 = [A_3] + [A_2] + [A_1] + [A_0] \quad (11)$$

$$[B]_0 = [B] + [A_2] + 2[A_1] + 3[A_0] \quad (12)$$

and at time $t = 0$

$$3[A_3]_0 = [B]_0 \quad (13)$$

yields

$$[B] - 3[A_3] = 2[A_2] + [A_1] \quad (14)$$

After substitution, eq 10 becomes

$$d[A]/dt = -3k_1[A_3][B] - k_2[B]([B] - 3[A_3]) \quad (15)$$

$$= 3(k_2 - k_1)[A_3][B] - k_2[B]^2 \quad (16)$$

Equation 16 is identical with eq 7.

The equation originally given by Frost and Schwemmer[29] for competitive consecutive second-order reaction holds only in cases where the second functional group is generated by the first reaction step. Otherwise, for a difunctional molecule B_2 the rate equation is given if $[A]_0 = [B]_0$ by

$$d[A]/dt = 2(k_2 - k_1)[A][B_2] - k_2[A]^2 \quad (17)$$

which for independent functional groups B ($k_1 = k_2$) transforms to a simple second-order rate expression.

Registry No. (Polypropylene glycol)·(tris(4-isocyanatophenyl)thiophosphate) copolymer, 88546-51-4.

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