

# Kinetic and statistical aspects of the formation of polyurethanes from toluene diisocyanate

Mirta I. Aranguren and Roberto J. J. Williams\*

*Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Juan B. Justo 4302, (7600) Mar del Plata, Argentina*

*(Received 20 March 1985; revised 19 July 1985)*

Kinetic and statistical aspects of the polymerization of toluene diisocyanate (TDI 80:20) with a commercial polyether polyol based on sorbitol have been analysed. The polymerization kinetics were measured under isothermal and adiabatic conditions, using different amounts of triethylamine (TEA) as catalyst. The kinetics were described by two independent second-order equations giving the reaction of *ortho*- and *para*-NCO groups. The activation energy for the reaction of *o*-NCO was significantly higher than that corresponding to *p*-NCO. Both activation energies decrease on increasing the catalyst concentration. For uncatalysed systems, *o*-NCO reacts 100 times slower than *p*-NCO at 25°C, while both reactivities become equivalent at temperatures close to 125°C. A general gelation condition was found using a recursive procedure. Systems polymerized with a high excess of TDI show evidence of isocyanurate ring formation, while OH-terminated prepolymers may be used to decrease the gel conversion and the time to gel at room temperature.

(Keywords: polyurethanes; toluene diisocyanate; kinetics; statistics; gelation; prepolymers; isocyanurate)

## INTRODUCTION

In spite of the industrial importance of polyurethanes prepared from toluene diisocyanate (TDI), few fundamental studies concerning kinetic and statistical aspects of network formation are available. In particular, a characteristic feature of the TDI molecule is the different reactivities of the *ortho*- and *para*-isocyanate groups, and the variation of reactivity with temperature. McGinn and Spaunburgh<sup>1</sup> reported that, at 25°C, the NCO group in the *para* position is 8–10 times as reactive as that in the *ortho* position, but at 100°C they are similar in reactivity. This result is frequently quoted in reviews on polyurethanes<sup>2,3</sup> but, to our knowledge, has not been investigated in detail. As a matter of fact, knowledge of the reactivity ratio and its dependence on temperature may be used to select operation conditions leading to a desired network structure.

The aim of this paper is to report kinetic and statistical results for the reaction of TDI with a commercial polyfunctional polyol. It will be shown that, once the reactivity ratio of *o*-NCO and *p*-NCO groups is determined as a function of temperature and catalyst level, statistical parameters (such as the gelation conversion) or kinetic requirements (such as the time to gel at room temperature) may be modified by changing the curing schedule.

## EXPERIMENTAL

### Materials

Toluene diisocyanate (99.9% purity) was available as a mixture of 80% 2,4- and 20% 2,6-isomers. It was reacted with a commercial polyfunctional polyether polyol based

on sorbitol (Voranol 466, Dow), which was carefully dehydrated at 120°C for 6 h before use, and had a equivalent weight of 139.8 g eq<sup>-1</sup> (OH value of 401.3 mg KOH g<sup>-1</sup>), as determined with a conventional acetylation technique. The catalyst was triethylamine (TEA), used in proportions ranging from 0 to 0.0105 g g<sup>-1</sup> polyol.

### Kinetics

The polymerization kinetics of stoichiometric amounts of both reactants were measured under isothermal and adiabatic conditions. The isothermal determinations were carried out by placing a small amount (~3 g) of uncatalysed mixture between thin aluminium foils. Several of these 'sandwiches' were placed between two heated metal plates held at temperatures lying in the 20–60°C range. The constancy of temperature during each run was controlled by inserting a thin copper-constantan thermocouple inside one of the 'sandwiches'. Samples were periodically withdrawn and quenched in a solution of dibutylamine in toluene. The amount of unreacted NCO groups was determined by back-titrating with HCl, using bromocresol green as indicator. The absence of catalyst and the low curing temperatures enabled the reaction to be followed up to conversions close to 60%.

In order to study the polymerization kinetics at high reaction rates (i.e. presence of catalyst and high temperatures), the adiabatic temperature rise technique was used. The reaction mixture, including the selected amount of catalyst, was intensively mixed for 15 s in a cylindrical vessel of 9.5 cm diameter and 10 cm height. A copper-constantan thermocouple was centred and its output continuously monitored with a data logger (Fluke 2200 B).

\* To whom all correspondence should be addressed.

### Critical gelation ratios

Samples with a known excess of one of the reactants (isocyanate or polyol) were prepared in order to determine the critical gelation ratio, i.e. the molar ratio leading to gelation at full reaction extent. The absence of a gel phase was ascertained when full solubility in methyl ethyl ketone (MEK) was observed. Some of the gelled samples were monitored with a Perkin-Elmer 599 i.r. spectrophotometer. The technique consisted of grinding the cured sample and making pellets with KBr.

## RESULTS AND DISCUSSION

### Kinetics

Figure 1 shows adiabatic temperature rise curves for four different catalyst concentrations. Corrections for heat losses<sup>4</sup> were found to be negligible up to temperatures limited by the horizontal bars. The adiabatic temperature rise may be estimated as  $\Delta T_{ad} = 155^\circ\text{C}$ .

The thermal energy balance in an adiabatic reactor may be written as

$$c_p \frac{dT}{dt} = -\Delta H \frac{dp}{dt} \quad (1)$$

where  $p$  is the reaction extent,  $dp/dt$  is the reaction rate,  $c_p$  is the specific heat and  $-\Delta H$  is the heat of reaction. As

$$\Delta T_{ad} = -\Delta H/c_p \quad (2)$$

the adiabatic temperature rise curves provide instantaneous values of reaction rate and reaction extent:

$$\frac{dp}{dt} = (dT/dt)/\Delta T_{ad} \quad (3)$$

$$p = (T - T_0)/\Delta T_{ad} \quad (4)$$

In order to regress the experimental curves, a kinetic model has to be proposed. Let us call  $p_A$  the reaction extent of OH groups,  $p_B$  the reaction extent of NCO

groups and  $r$  the initial ratio of OH groups to NCO groups. Both reaction extents are related by

$$p_B = r p_A \quad (5)$$

For a stoichiometric mixture,  $r = 1$  and  $p_A = p_B = p$ .

It is necessary to identify separately the conversion of NCO groups located in *ortho* and *para* positions of the toluene ring. The conversion of *o*-NCO groups will be denoted by  $q_1$  while  $q_2$  will represent the conversion of *p*-NCO groups. As the TDI 80:20 contains 60% of *o*-NCO and 40% of *p*-NCO groups, the overall conversion of NCO groups is given by

$$p_B = 0.6q_1 + 0.4q_2 \quad (6)$$

A second-order kinetic equation is proposed for the consumption of each kind of NCO group. Thus,

$$-d[o\text{-NCO}]/dt = k_1[o\text{-NCO}][\text{OH}] \quad (7)$$

$$-d[p\text{-NCO}]/dt = k_2[p\text{-NCO}][\text{OH}] \quad (8)$$

Or, in terms of conversions,

$$dq_1/dt = A_1[\text{OH}]_0 \exp(-E_1/RT)(1-q_1)(1-p) \quad (9)$$

$$dq_2/dt = A_2[\text{OH}]_0 \exp(-E_2/RT)(1-q_2)(1-p) \quad (10)$$

And, from equation (6),

$$\frac{dp}{dt} = 0.6 \frac{dq_1}{dt} + 0.4 \frac{dq_2}{dt} \quad (11)$$

The initial concentration of OH groups for a stoichiometric mixture is  $[\text{OH}]_0 = 4.905 \times 10^{-3} \text{ eq cm}^{-3}$ .

Once a set of  $(A_1, E_1, A_2, E_2)$  values is selected, the evolution of  $q_1$ ,  $q_2$  and  $p$  may be obtained by numerical integration of equations (9) to (11), using a fourth-order Runge-Kutta method. From the  $p$  vs.  $t$  information, the corresponding  $T$  vs.  $t$  curve may be obtained from equation (4). The best set of kinetic parameters, defined as the one minimizing the integral

$$I = \int (T_{\text{pred}} - T_{\text{exp}})^2 dt \quad (12)$$

was obtained using a nonlinear regression technique<sup>5</sup>.

An excellent fit could be obtained for every run, as is illustrated in Figure 2 for the case with the highest catalyst concentration. Table 1 shows the best set of kinetic parameters as well as the maximum reaction extent used in the regression analysis (limited by the accuracy of experimental information with respect to heat losses).

The rate equations derived from the adiabatic analysis were tested with runs carried out under isothermal conditions. Figure 3 shows conversion vs. time curves at three different temperatures for uncatalysed samples. The good agreement between experimental and predicted conversions ensures the validity of the kinetic parameters regressed from the adiabatic runs.

Returning to Table 1, it may be seen that both activation energies decrease with increase of the catalyst concentration. As could be expected, the activation energy for the reaction of the *p*-NCO group,  $E_2$ , lies in a

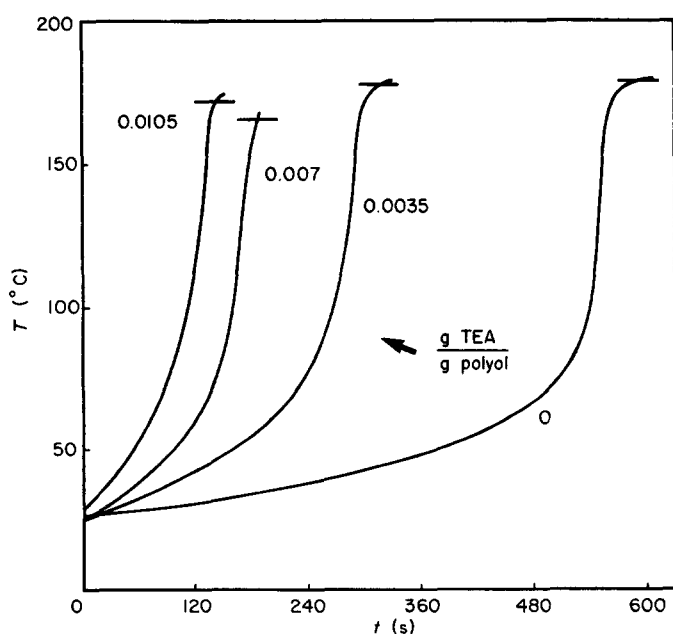


Figure 1 Adiabatic temperature rise curves for different catalyst concentrations. Horizontal bars indicate the maximum temperature used in the regression analysis

typical range of values reported for polyurethanes<sup>4</sup>. However, due to steric hindrance provoked by the methyl group, the *o*-NCO requires a higher activation energy,  $E_1$ , to react.

The ratio between the specific rate constants of *p*-NCO ( $k_2$ ) and *o*-NCO groups ( $k_1$ ) is shown in Figure 4 as a function of temperature. At 25°C, the ratio  $k_2/k_1$  is close to 100 for uncatalysed samples, and equal to 32.5 for the sample with the highest amount of catalyst. For both samples, the ratio is close to 1 at 125°C. The significant influence of temperature on the way in which the TDI molecule reacts is also illustrated in Figure 5. Here, the conversion of *p*-NCO groups ( $q_2$ ) and *o*-NCO groups ( $q_1$ ) has been plotted as a function of the overall conversion of NCO groups ( $p_B$ ), for two different reaction temperatures and using the kinetic parameters of uncatalysed samples. Clearly, at room temperature the *o*-NCO practically does not react until the concentration of *p*-NCO groups has been sufficiently depleted. However, at 140°C *o*-NCO reacts more rapidly than *p*-NCO. Obviously, this implies very different structures of the resulting polyurethane networks.

#### Gelation

Knowledge of the gelation condition is important not only for the design of a particular polymerization process but also because the experimental determination of the critical gelation ratio (in an excess of OH or NCO groups) provides additional information to characterize the thermosetting system.

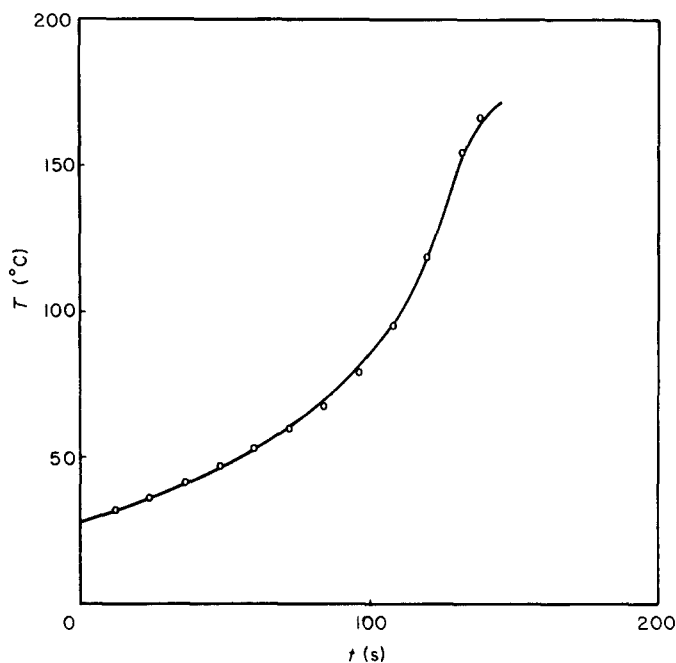


Figure 2 Fit of an adiabatic temperature rise curve with the proposed kinetic model. Points are experimental values while the full curve represents the best regression

Table 1 Best set of kinetic parameters and limiting conversion used in the regression

g TEA/g polyol	$A_1$ ( $\text{cm}^3 \text{eq}^{-1} \text{s}^{-1}$ )	$E_1$ ( $\text{kcal mol}^{-1}$ )	$A_2$ ( $\text{cm}^3 \text{eq}^{-1} \text{s}^{-1}$ )	$E_2$ ( $\text{kcal mol}^{-1}$ )	$p_{\text{max}}$
0	$4.75 \times 10^{15}$	25.457	$1.10 \times 10^{10}$	15.049	0.99
0.0035	$3.87 \times 10^{12}$	20.363	$1.81 \times 10^8$	11.907	0.99
0.0070	$6.34 \times 10^{11}$	18.565	$1.46 \times 10^7$	10.122	0.91
0.0105	$1.66 \times 10^{10}$	16.118	$1.82 \times 10^6$	8.656	0.93

The derivation of the gelation condition is given in the Appendix. The result is

$$r = q_1(f_c - 1)(0.2q_1 + 0.8q_2) \quad (13)$$

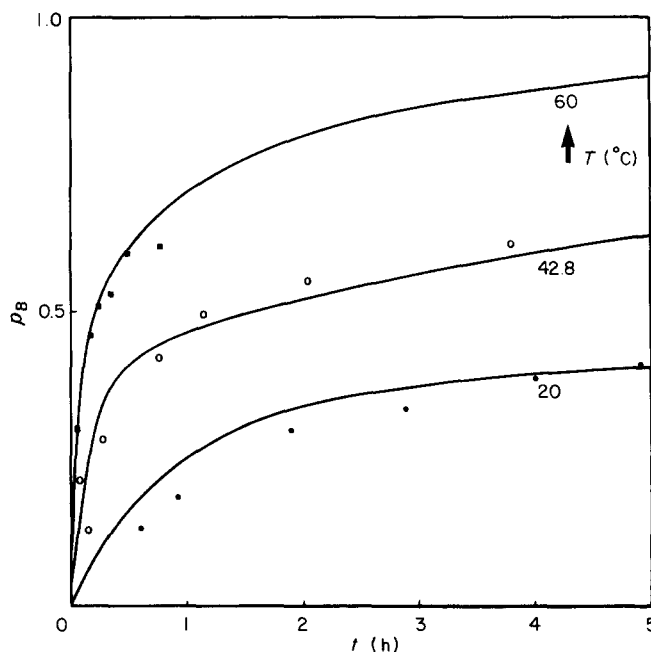


Figure 3 Conversion of NCO groups vs. time at three different temperatures for uncatalysed samples. Points are experimental values while full curves are predicted results using the kinetic parameters derived in the adiabatic analysis

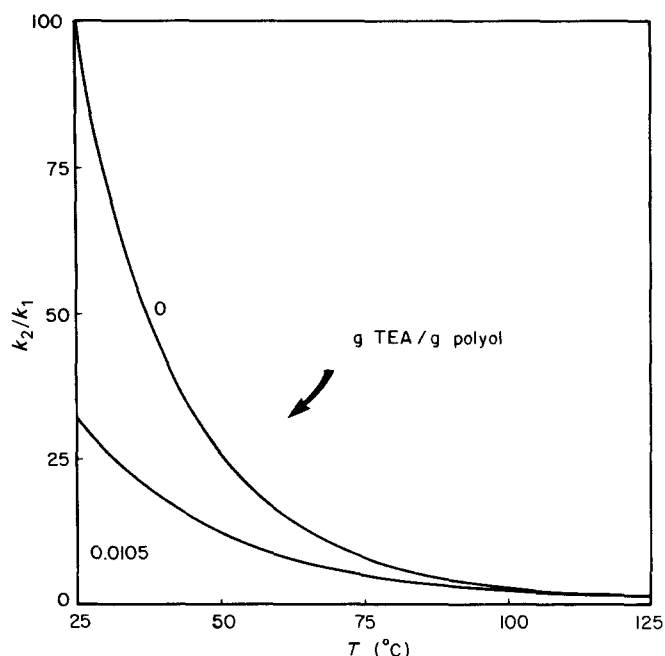


Figure 4 Ratio of specific rate constants of *p*-NCO ( $k_2$ ) and *o*-NCO ( $k_1$ ) as a function of temperature, for two different catalyst concentrations

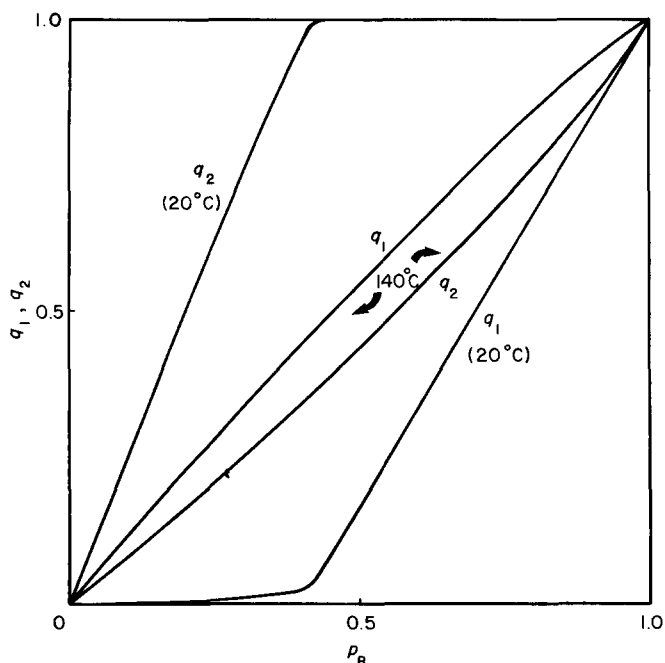


Figure 5 Conversion of *p*-NCO groups ( $q_2$ ) and *o*-NCO groups ( $q_1$ ) as a function of the overall conversion of NCO groups ( $p_B$ ), for uncatalysed samples at two different temperatures

where  $f_c$  is the weight (or functionality) average functionality of the polyol.

The experimental determination of the critical gelation ratio for samples prepared with an excess of polyol was performed at 60°C in the absence of catalyst. Samples were reacted for 1–2 days, attaining complete conversion. The resulting critical ratio was

$$r_c(\text{excess of OH}) = 3.25 \pm 0.15 \quad (14)$$

For  $r > r_c$  samples were completely soluble at the end of the reaction, while for  $1 < r < r_c$  a gel fraction was always present. As the NCO groups were completely reacted,  $q_1 = q_2 = 1$ . Then, from equation (13), the value of  $f_c$  may be obtained as

$$f_c = 4.25 \pm 0.15 \quad (15)$$

On the other hand, the critical gelation ratio for an excess of NCO groups may, in principle, be used to obtain the reactivity ratio  $k_2/k_1$  at different temperatures. At full conversion of OH groups,  $p_A = 1$  and  $p_B = r$  (equation (5)). Then, from equation (6),

$$r_c(\text{excess of NCO}) = 0.6q_1 + 0.4q_2 \quad (16)$$

Dividing equation (9) by equation (10) and integrating leads to

$$(1 - q_1) = (1 - q_2)^{k_1/k_2} \quad (17)$$

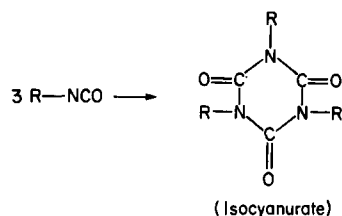
Also, from equations (13) and (15),

$$r_c(\text{excess of NCO}) = 3.25q_1(0.2q_1 + 0.8q_2) \quad (18)$$

Once  $r_c(\text{excess of NCO})$  is experimentally measured at a particular temperature, equations (16) to (18) may be used to determine  $q_1$ ,  $q_2$  and  $k_1/k_2$ . Figure 6 shows the predicted functionality between  $r_c(\text{excess of NCO})$  and

$k_1/k_2$ . A good sensitivity is observed in the range  $0.05 < k_1/k_2 < 0.6$ . For example, at  $T = 42.8^\circ\text{C}$ , Figures 4 and 6 predict a critical gelation ratio  $r_c(\text{excess of NCO}) = 0.513$  for uncatalysed samples. Samples with a higher NCO content, i.e.  $r < r_c$ , would have to be completely soluble at the end of the reaction. However, experimental runs at this temperature did not agree with these predictions. The existence of a gel phase, even in small amounts, was observed for ratios as low as  $r = 0.2$ . The same happened for other reaction temperatures. In order to interpret these experimental results, an i.r. analysis of the gel phase was carried out. Figure 7 shows the i.r. spectrum of the gel resulting from the uncatalysed reaction carried out at 42.8°C and  $r = 0.2$ . According to Merten *et al.*<sup>6</sup>, the following assignment of peaks may be made: 2240–2270  $\text{cm}^{-1}$ , remaining NCO groups; 1690–1720  $\text{cm}^{-1}$ , urethane groups; 1420  $\text{cm}^{-1}$  (marked with an arrow in Figure 7), isocyanurate ring. There is no evidence of allophanate groups (peak at 1653–1708  $\text{cm}^{-1}$ ) or urea linkages (peak at 1640  $\text{cm}^{-1}$ ). Furthermore, when  $r$  is increased the peak ascribed to the isocyanurate ring decreases in intensity. For  $r > 0.5$  it vanishes from the spectrum.

Then, when the polymerization of TDI with a polyol is carried out in a great excess of NCO groups, the following secondary reaction takes place:



This reaction increases the functionality of species carrying NCO groups and, consequently, leads to the

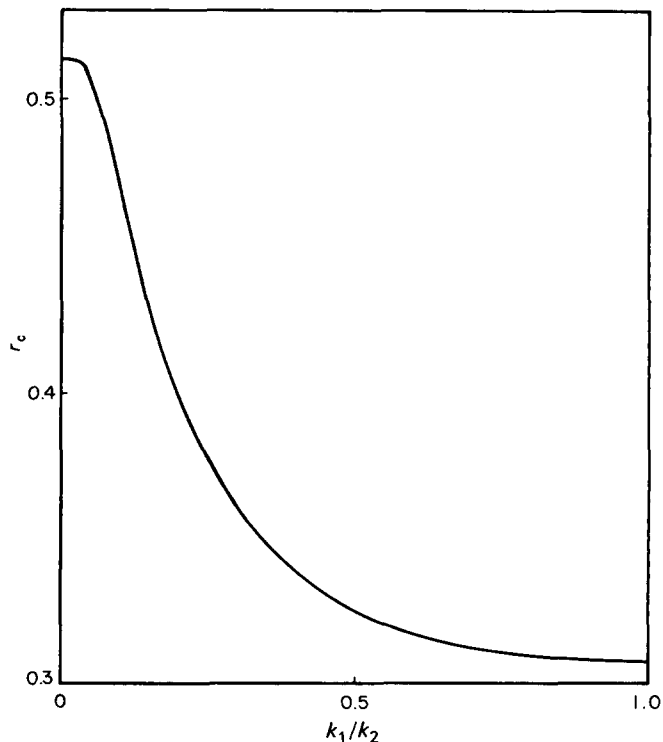


Figure 6 Critical gelation ratio in excess of NCO groups as a function of the ratio of specific rate constants of *o*-NCO ( $k_1$ ) and *p*-NCO ( $k_2$ )

formation of the observed gel phase in samples prepared with a high isocyanate excess.

Because of the change of reactivity ratio with temperature (Figure 4), equation (13) will be verified at overall reaction extents varying with the polymerization temperature. Table 2 shows the gelation conversion,  $p_{\text{gel}}$ , for uncatalysed stoichiometric samples reacted at different temperatures. The minimum  $p_{\text{gel}}$  is obtained for  $k_1 = k_2$  ( $T$  close to 125°C).

#### Formation of prepolymers

For several applications, it is convenient to carry out the polymerization in two steps. First, a prepolymer is produced working with an excess of one of the reactants. Then, the reactant in deficit is added in a proportion leading to overall stoichiometry, and the reaction is carried out to completion. The reasons for this procedure are to reduce the vapour pressure of the reactant containing NCO groups (preparing a prepolymer with an isocyanate excess), and to shorten the gel time at room temperature (by increasing the functionality of the prepolymer). The latter possibility may be important for polyurethanes used as coatings or in cold-box applications for the foundry industry. Let us look at this possibility in more detail.

As previously shown, a sample containing a polyol excess, such that  $r > 3.25$ , will be a liquid at complete conversion. Its viscosity, related to the weight average molecular weight, will depend on the departure of  $r$  from 3.25. The closer it is to the critical value, the higher the viscosity. The weight (or functionality) average functionality of such a prepolymer may be obtained from

statistical analysis. This leads to<sup>7</sup>

$$f_c^* = 1 + [(r-1)(f_c-1)]/[r-(f_c-1)] \quad (19)$$

If a stoichiometric imbalance  $r=5$  is selected, equation (19) gives  $f_c^* = 8.43$ . If the necessary amount of TDI (80:20) leading to a stoichiometric system is added, and the polymerization is carried out at 20°C without catalyst, it is found that gelation takes place at  $p_B = 0.497$  in  $t_{\text{gel}} = 1.7$  days. These figures may be compared with  $p_B = 0.612$  and  $t_{\text{gel}} = 4.44$  days for the same reaction starting from the original polyol, i.e. without using a prepolymer. Obviously, the time to gel may be shortened by using a convenient amount of catalyst. For example, starting from the same prepolymer ( $f_c^* = 8.43$ ) and TDI (80:20), and using 0.0105 g TEA/g polyol, leads to the formation of a gel in  $t_{\text{gel}} = 1$  h. In these conditions, TDI may replace other isocyanates, like MDI, in room-temperature applications.

#### CONCLUSIONS

The polymerization kinetics of TDI with a polyol may be described by two independent equations representing the consumption of each of the distinguishable *o*- and *p*-NCO groups. Both equations show second-order kinetics (first order with respect to each one of the reactants). The activation energy for the reaction of *p*-NCO groups has similar values as those reported in the literature for polyurethanes formed from unrestricted NCO groups, i.e. activation energies close to 10 kcal mol<sup>-1</sup>. However, the activation energy for the reaction of *o*-NCO groups is significantly higher, i.e. close to 20 kcal mol<sup>-1</sup>, due to steric hindrance provoked by the neighbouring methyl group. Both activation energies decrease on adding a convenient catalyst. The ratio of specific rate constants for the reaction of both types of NCO groups depends on temperature and catalyst concentration. For uncatalysed systems *o*-NCO reacts 100 times slower than *p*-NCO at 25°C, and both reactivities become equivalent at temperatures close to 125°C. Adding a catalyst decreases the difference in reactivities at room temperature while practically not altering the temperature at which both reactivities become the same.

When the polymerization is carried out using a high excess of TDI, i.e. to form an NCO-terminated prepolymer, a secondary reaction leading to isocyanurate rings takes place. Associated with this reaction is the presence of a gel fraction. On the other hand, OH-terminated prepolymers, obtained with an excess of polyol, may be used to decrease the gel conversion and the time to gel at room temperature.

#### ACKNOWLEDGEMENTS

The authors wish to thank the Secretaria de Estado de Ciencia y Tecnología (SECYT, Argentina) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC, Argentina) for financial support.

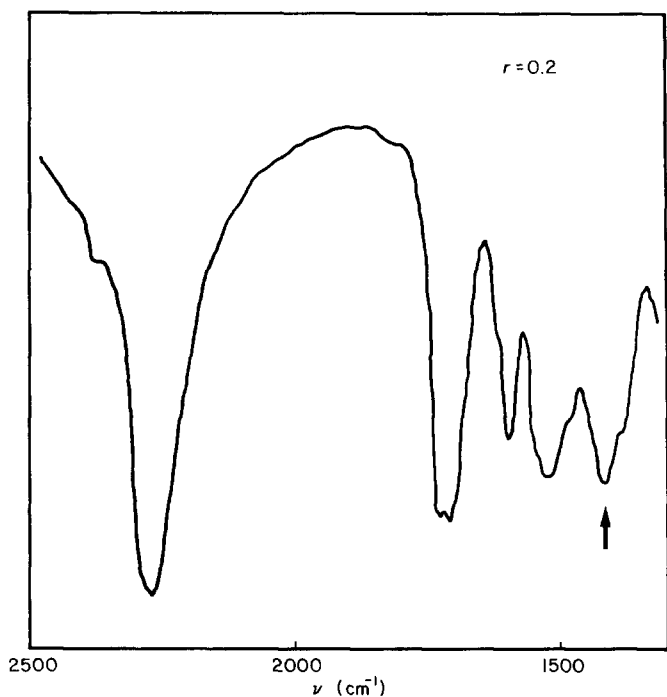


Figure 7 I.r. spectrum of the gel phase resulting from the reaction at 42.8°C of an uncatalysed sample with  $r=0.2$  (for meaning of arrow, see text)

Table 2 Gelation conversion for uncatalysed stoichiometric samples reacted at different temperatures

$T$ (°C)	20	60	80	110	130	140	170
$p_{\text{gel}}$	0.6120	0.6118	0.6012	0.5637	0.5543	0.5563	0.5763

## APPENDIX

In order to derive the gelation condition it is necessary to describe the polyol structure. It may be considered as composed of molecules  $A_{f,i}$  showing a distribution of sizes  $i$  and functionalities  $f$  (number of OH groups per molecule). Let us assume that the polymerization has taken place to a reaction extent  $p_A$  of OH groups and  $p_B = r p_A$  of NCO groups (conversion of *o*-NCO groups =  $q_1$ , conversion of *p*-NCO groups =  $q_2$ ). The recursive method developed by Miller and Macosko<sup>8</sup> may be now applied.

The average weight hanging from an OH group when looking out from its parent molecule may be written as

$$E(W_{OH}^{out}) = p_A [(0.4q_2/p_B)E(W_{p-NCO}^{in}) + (0.6q_1/p_B)E(W_{o-NCO}^{in})] \quad (A.1)$$

This results from the fact that, if the OH group has not reacted, an event with probability  $(1 - p_A)$ , the hanging weight is zero. If it has reacted, an event with probability  $p_A$ , the average weight is given by the expression between brackets. The factor  $(0.4q_2/p_B)$  gives the fraction of reacted *p*-NCO groups with respect to the overall conversion of NCO groups (probability that a reacted NCO is a *p*-NCO). Similarly, the factor  $(0.6q_1/p_B)$  represents the fraction of converted *o*-NCO groups with respect to the overall conversion of NCO functionalities.  $E(W_{p-NCO}^{in})$  and  $E(W_{o-NCO}^{in})$  are, respectively, the average weights hanging from a *p*-NCO and an *o*-NCO when looking into its parent molecule. They may be written as

$$E(W_{p-NCO}^{in}) = M_B + E(W_{o-NCO}^{out}) \quad (A.2)$$

$$E(W_{o-NCO}^{in}) = M_B + \frac{1}{3}E(W_{o-NCO}^{out}) + \frac{2}{3}E(W_{p-NCO}^{out}) \quad (A.3)$$

$M_B$  is the molecular weight of the TDI molecule, and the factors  $\frac{1}{3}$  and  $\frac{2}{3}$  represent, respectively, the fraction of *o*-NCO groups in 2,6-TDI and 2,4-TDI molecules of the TDI (80:20).  $E(W_{o-NCO}^{out})$  and  $E(W_{p-NCO}^{out})$  are, respectively, the average weights hanging from *o*-NCO and *p*-NCO groups when looking out from its parent molecule. They are given by

$$E(W_{p-NCO}^{out}) = q_2 E(W_{OH}^{in}) \quad (A.4)$$

$$E(W_{o-NCO}^{out}) = q_1 E(W_{OH}^{in}) \quad (A.5)$$

If the *p*-NCO group has not reacted, an event with probability  $(1 - q_2)$ , the average weight is zero. If it has reacted, an event with probability  $q_2$ , the weight is  $E(W_{OH}^{in})$ , i.e. the average weight hanging from an OH group when looking into its parent molecule. The reasoning is similar for the *o*-NCO group. Finally, if we call  $A_f = \sum_i A_{f,i}$ , the number of polyol molecules with functionality  $f$ , and  $a_{f,i} = A_{f,i}/A_f$ , the mole fraction of polyol molecules with size  $i$  belonging to the group with functionality  $f$ ,  $E(W_{OH}^{in})$  may be written as

$$E(W_{OH}^{in}) = \sum_f \left[ f A_f / \left( \sum_f f A_f \right) \right] \sum_i a_{f,i} [M_{A_{f,i}} + (f - 1)E(W_{OH}^{out})] \quad (A.6)$$

$M_{A_{f,i}}$  is the molecular weight of a generic polyol molecule with functionality  $f$  and size  $i$ . By defining

$$M_{n,f} = \sum_i a_{f,i} M_{A_{f,i}} \quad (A.7)$$

as the number average molecular weight of the group of polyol molecules with generic functionality  $f$ ,

$$M_A = \left( \sum_f f A_f M_{n,f} \right) / \left( \sum_f f A_f \right) \quad (A.8)$$

as an average molecular weight of the polyol molecules, and

$$f_e = \left( \sum_f f^2 A_f \right) / \left( \sum_f f A_f \right) \quad (A.9)$$

as the weight (or functionality) average functionality of the polyol molecules, equation (A.6) may be rewritten as

$$E(W_{OH}^{in}) = M_A + (f_e - 1)E(W_{OH}^{out}) \quad (A.10)$$

A system of six equations (A.1) to (A.5) and (A.10) in six unknowns,  $E(W)$ , has been obtained with the recursive procedure. The gelation condition results when all the average weights,  $E(W)$ , become infinite. Solving the six equations it is found that this criterion is fulfilled when

$$r = q_1 (f_e - 1) (0.2q_1 + 0.8q_2) \quad (A.11)$$

Equation (A.11) contains the gelation criterion for an ideal polymerization as a particular case. Thus, when the reactivities of *o*-NCO and *p*-NCO are the same,  $q_1 = q_2 = p_B$  (equation (6)). With the aid of equation (5), equation (A.11) leads to

$$(p_A p_B)_{gel} = 1 / (f_e - 1) \quad (A.12)$$

which is the gelation condition for the polymerization of bifunctional and  $f_e$ -functional reactants in the absence of unequal reactivity or substitution effects.

## REFERENCES

- 1 McGinn, C. E. and Spaunburgh, R. G. 'Symposium on Isocyanate Polymers', American Chemical Society Meeting, Atlantic City, N.J., Sept. 1956
- 2 Frisch, K. C. in 'Polyurethane Technology', (Ed. P. F. Bruins), Interscience, New York, 1969, p. 3
- 3 Gmitter, G. T., Fabris, H. J. and Maxey, E. M. in 'Plastic Foams', Part I, (Eds. K. C. Frisch and J. H. Saunders), Marcel Dekker, New York, 1972, p. 127
- 4 Marciano, J. H., Rojas, A. J. and Williams, R. J. J. *Polymer* 1982, **23**, 1489
- 5 Stenstrom, M. K., Brown, L. C. and Hwang, H. J. J. *Environ. Eng. Div. ASCE* 1981, **107**, 379
- 6 Merten, R., Laurerer, D., Braun, G. and Dahm, M. *Makromol. Chem.* 1967, **101**, 337
- 7 Miller, D. R., Vallés, E. M. and Macosko, C. W. *Polym. Eng. Sci.* 1979, **19**, 272
- 8 Miller, D. R. and Macosko, C. W. *Macromolecules* 1978, **11**, 656