Effect of the ratio of reactive groups on gelation and cyclization during polyurethane network formation

J. Budinski-Simendić* and Z. S. Petrović
Faculty of Technology, University of Novi Sad, 21000 Novi Sad, Yugoslavia

and M. Ilavský† and K. Dušek
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 16206 Prague 6, Czech Republic
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The effect of the initial molar ratio of the reactive groups, r_{NCO} ($=[NCO]_0/[OH]_0=1.0$ or 0.8), on the gelation of polyurethane networks based on tris(4-isocyanatophenyl)thiophosphate and poly(oxypropylene) diol, was studied. The number-average molecular weight, $\bar{M}_n$, in the pre-gel state, the critical conversion at the gel point, p^c_{NCO}, and the critical ratio, r^c_{NCO}, at which gelation occurs, were measured. The decrease in $1/r^c_{NCO}$ with increasing dilution in xylene suggests that cyclization takes place. The experimental $\bar{M}_n$ values are always lower than the theoretical ones, with the latter being calculated for the ring-free case. The fraction of bonds that are lost in the cyclization process, s, calculated from the difference between the experimental and theoretical values of $\bar{M}_n$, increases with conversion and has a value near the gel point of 0.04–0.06. It is demonstrated both theoretically and experimentally that the values of s calculated from the shift of the gel point conversion are not equivalent to those obtained from $\bar{M}_n$, but depend on r_{NCO}.

(Keywords: polyurethane networks; gel point conversion; poly(oxypropylene)diol; molecular weight averages)

INTRODUCTION

It is well known that the reaction between monomers having a functionality greater than two leads to crosslinking and gel formation at a specific conversion level[1]. Intermolecular branching reactions are always accompanied by intramolecular reactions (i.e. cyclization). The extent of cyclization depends on many factors (e.g. functionality of components, flexibility of sequences, etc.), but, in particular, to a large extent on the mechanism of network formation. The amount of cyclization that occurs is relatively low for step reactions[2] but it can become dominant in certain types of reaction, for example, in free-radical crosslinking polymerization[3].

The formation of polyurethane networks from aromatic diisocyanates and polyols which takes place by an alternating mechanism is a reaction in which the extent of cyclization is small[2]. Theoretical models exist that take cyclization into account, such as the rate model which only considers the formation of the smallest possible rings[4], the 'spanning-tree' approximation (as part of the theory of branching processes)[5] and computer simulations of structure growth in three-dimensional space[6–9]. However, the simplest determination of the extent of cyclization comes from the comparison of experimental results with those predicted by theories which describe the ring-free case. In the case of equal reactivity of the functional groups, and in the absence of any intramolecular reactions, the gel point can be predicted by using one of a number of theories of gelation[1,2,10–13].

In the statistical methods of network generation from units A and B (corresponding to the formation of polyurethane networks from polyols and isocyanates), the gel point condition is given by the equation[10].

$$p^c_A p^c_B = r_B (p^c_B)^2 = (p^c_A)^2 / r_B = [(f_{w,A}-1)(f_{w,B}-1)]^{-1} \quad (1)$$

where p^c_A and p^c_B are the critical gel point conversions of groups of type A and type B, respectively, and $f_{w,A}$ and $f_{w,B}$ are the corresponding 'weight-average' functionalities of the monomers, defined by the relationship

$$f_w = \sum_{i=1}^{f} i^2 n_i \Big/ \sum_{i=1}^{f} i n_i \quad (2)$$

where n_i is the number fraction of molecules of functionality i and r_B ($=[B]_0/[A]_0$) is the initial molar ratio of groups B and A (in fact, $r_B = p_A/p_B$). However, in the case of real systems, a shift of the gel point to higher conversions is observed, as a result of intramolecular reactions. In the case of polyurethanes, a shift to lower conversions, due to various side reactions (such as allophanate formation) can also be expected[14–18] (especially for networks prepared using excess amounts of the isocyanate component).

The intensity of intramolecular reactions increases with dilution of the system and should be at its lowest when the synthesis is carried out undiluted, i.e. in the bulk[19–21].

* Present address: Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 16206 Prague 6, Czechoslovakia
† To whom correspondence should be addressed

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Since intramolecular reactions do not lead to an increase in the molecular weight, the amount of groups that are 'wasted' in such reactions can be estimated by measuring the changes in the molecular weight with conversion in the pre-gel state and comparing these changes with those obtained from theoretical ring-free predictions. Measurement of the number-average molecular weight, $\bar{M}_n$, is particularly useful, since the experimental precision is high for the low molecular weights that are encountered in these systems and, moreover, the result is independent of the structure growth process[2-4]. Any ring-free theory predicts the $\bar{M}_n$ dependence on conversion to have the following form:

$$\bar{M}_n = \frac{n_A M_A + n_B M_B}{1 - (p_A f_{n,A} n_A + p_B f_{n,B} n_B)/2} \quad (3)$$

where n_A and n_B are the molar fractions, M_A and M_B are the molecular weights, and $f_{n,A}$ and $f_{n,B}$ are the number-average functionalities, of monomers A and B, respectively. The latter are given by:

$$f_n = \sum_{i=1}^{f} i n_i \Big/ \sum_{i=1}^{f} n_i \quad (4)$$

In equation (3), the numerator is equivalent to the average weight of a monomer unit and the denominator is equivalent to the number of molecules per monomer unit. The latter quantity is obtained by subtracting the number of bonds which connect the monomer units from the total number of units. This reasoning is valid for any ring-free case, in contrast to the gel point, which depends on the reactivities of the groups, etc.

As can be seen from equation (1), the extent of cyclization can also be estimated from the difference between the calculated and experimentally determined critical conversions at the gel point, i.e. p_A^c or p_B^c (at a given constant value of r_A). The use of the critical molar ratio (*CMR*) method is also possible: this consists in finding the initial critical ratio of the reactive groups, r_B^c ($=([B]_0/[A]_0)^c = p_A^c/p_B^c$), at which gelation occurs when the conversion of the 'minority' groups approaches 100%. For an ideal case, involving the reaction of a bifunctional monomer A ($f_{n,A} = f_{w,A} = 2$) and a trifunctional monomer B ($f_{n,B} = f_{w,B} = 3$), it follows, from equation (1), that

$$p_A^c p_B^c = 1/2 \quad (5)$$

and $r_B^c = 2$ (if $p_A^c = 1$, i.e. excess of monomer B), or 0.5 (if $p_B^c = 1$, i.e. excess of monomer A).

The dependence of r_B^c on dilution at network formation is a proof of cyclization[20]. In the case of a bimolecular reaction, the probability of an intramolecular reaction to occur is proportional to the product of the local concentrations of unreacted functional groups from the same molecule, whereas the probability of an intermolecular reaction taking place is determined by the product of the local concentration of the selected molecule and the average concentration of the bifunctional groups. This latter concentration decreases with dilution, so that the relative probability of cyclization therefore increases. Thus, the dependence of r_B^c on the dilution at network formation, and the extrapolation to a hypothetical 'infinite concentration' of reactive groups, can be used for estimation of the cyclization (from the slope) and the average functionality $f_{w,i}$, plus differences or changes in reactivities of the functional groups in monomer A or B. If the reactivity of the second group increases when the first one has already reacted (the positive substitution effect) the value of $1/r_B^c$ is higher than 2, and vice versa. In addition, the critical gel point conversions (p_A^c or p_B^c) are affected by the substitution effect, e.g. a positive substitution effect decreases the values of these critical conversions, and vice versa. It is important that equation (3) is not affected by the reactivity difference, because $\bar{M}_n$ depends only on the number of bonds, and not on their distribution among the molecules, as in the case of the gel point.

In this work, we have studied the effect of the initial molar ratio of the reactive groups, r_{NCO} ($=[NCO]_0/[OH]_0$), and the dilution on conversion at the gel point and in the pre-gel region on the increase of the number-average molecular weights. We have used poly(oxypropylene)diol (monomer A) and tris(4-isocyanatophenyl)thiophosphate (monomer B). The advantages of this system are as follows: both components are compatible after melting of the triisocyanate, the reaction at room temperature is slow, allowing sufficient time for handling, and the end groups in both components are far apart, so that the reactivities of other groups in the molecule should not be affected after one of the groups has reacted. Stoichiometric ratio or an excess of hydroxyl groups have been used in all of the experiments. The results were interpreted, both in terms of cyclization and also in possible intrinsic differences in reactivity of the functional groups.

EXPERIMENTAL

Materials

Poly(oxypropylene)diol (PD), purchased from the Aldrich Chemical Company, was dried by azeotropic distillation with benzene. The hydroxyl content was determined by reaction with excess of phenyl isocyanate; the unreacted isocyanate was then measured by reaction with dibutylamine, and the excess of dibutylamine was determined by potentiometric titration with 0.1 M HCl. Using this method the PD was found to contain 3.5 wt% of OH groups. The number-average molecular weight, $\bar{M}_{PD}$, determined by vapour phase osmometry) (v.p.o.), was 970, so that the number-average functionality, $f_{n,PD}$, was 2. The water content (determined by coulometry) was 0.002 wt%. Tris(4-isocyanatophenyl)thiophosphate (TI) (Desmodur RF, $M_{TI} = 465$) was purchased from Bayer (Germany). Purification of the isocyanate, which is supplied as a 20 wt% solution in methylene chloride, was carried out by recrystallization from this same (concentrated) solution. The NCO content, determined by titration, corresponded to a theoretical value of M_{TI} of 465, so that the value of $f_{n,TI}$ was equal to 3.

Methods of preparation and measurements

The synthesis of polyurethanes in the pre-gel stage was carried out at room temperature. The isocyanate and polyol were placed in a three-necked flask, and the temperature was raised to 90°C in order to melt the isocyanate. As soon as the mixture became clear, the sample was cooled to room temperature and the polymerization was allowed to continue until gelation occurred. It was found (by titration) that ≈30% of the NCO groups reacted during this initial period. Samples

for determination of the molecular weight and the NCO content were removed from the flask at different times. A portion of such a sample was dissolved in methanol in order to stop any further reaction, and the solvent was subsequently removed under vacuum at ≈50°C over a period of several weeks, and then used for $\bar{M}_n$ determination. The other part of the sample was used for determination of the conversion of the isocyanate groups, p_{NCO}, by the use of titration. Samples were prepared at two initial ratios of reactive groups, with $r_{NCO} = [NCO]_0/[OH]_0 = 1.0$ and 0.8.

Samples of solutions and networks for the determination of the critical ratio of the reactive groups were prepared by reaction in bulk and in xylene solutions (0–60 vol%) at 80°C, using dibutyltin dilaurate (≈0.01 wt%) as the catalyst. The reaction was allowed to continue for 2 days in sealed ampoules, and under a nitrogen atmosphere. The critical value, r^c_{NCO}, was determined by extraction of the reacted samples with xylene, with this value taken as being between the values of r_{NCO} for the last completely soluble sample and the first sample that contained some fraction of gel (*Table 1*).

Experimental values of the number-average molecular weights ($\bar{M}_{nb}$) of methanol-blocked samples were measured at 90°C by using a Knauer vapour pressure osmometer, with toluene as the solvent. The values of $\bar{M}_{nb}$ thus obtained were higher than those of the polymer itself and therefore corrected experimental values of the molecular weight ($\bar{M}_{ne}$) were calculated, by subtracting the weight corresponding to the reacted methanol, as follows:

$$\bar{M}_{ne} = \bar{M}_{nb} - \frac{f_{n,TI} f_{n,PD} r_{NCO} M_{CH_3OH}(1 - p_{NCO})}{f_{n,PD} r_{NCO} + f_{n,TI} - f_{n,TI} f_{n,PD} r_{NCO} p_{NCO}} \quad (6)$$

where M_{CH_3OH} (= 32) is the molecular weight of methanol.

The conversions of the isocyanate groups, p_{NCO}, were calculated from the amount of NCO groups that had reacted. The free NCO groups were reacted with an excess of dibutylamine and the unreacted dibutylamine was then titrated with 0.1 M HCl.

Experimental values of the critical conversions at the gel point p^c_{NCO} were determined by using the solubility method. The solubility of the mixtures in methanol was tested at different reaction time intervals, and at the same time, the conversion was determined by titration. The experimental p^c_{NCO} values were obtained by interpolation, being taken as the value found at the mid point of the time interval between the last fully soluble sample and the first sample that was found to contain an insoluble component.

RESULTS AND DISCUSSION

Critical molar ratio of reactive groups

As has been pointed out in the Introduction, the extrapolation of the dependence of the critical molar ratio r^c_{NCO} on dilution to the 'infinite' concentration (c) of reactive groups, i.e. for $\lim c^{-1} = 0$, can be used for checking the functionality and reactivity assumptions. The volume concentration of functional groups in the presence of a diluent (xylene) is given by

$$c = (V_{TI} c_{NCO} + V_{PD} c_{OH})/2(V_{TI} + V_{PD} + V_X) \quad (7)$$

where c_{NCO} and c_{OH} are the respective molar concentrations of the NCO and OH groups in triisocyanate (TI) and diol (PD), and V_{TI}, V_{PD} and V_X are the volumes of TI, PD and xylene, respectively. *Figure 1* shows the plot of $1/r^c_{NCO}$ as a function of c^{-1}. Due to the occurrence of cyclization, the values of $1/r^c_{NCO}$ decrease linearly with c^{-1} (i.e. with increasing dilution), with the slope of this dependence being a measure of the extent of cyclization[18].

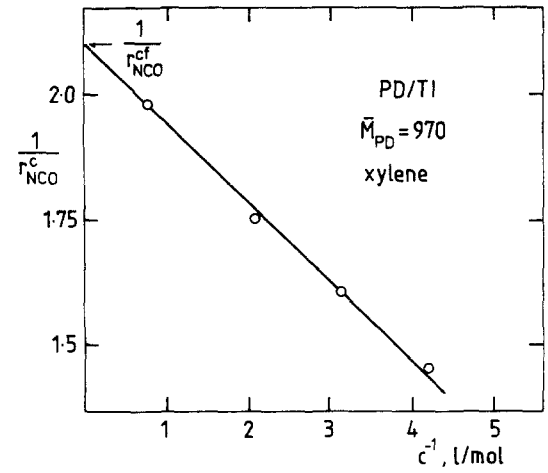

Figure 1 Dependence of the reciprocal critical molar ratio of the reactive groups, $1/r^c_{NCO}$, on the reciprocal concentration of the functional groups at network formation, c^{-1}, for the PD/TI system in xylene

By extrapolation of $1/r^c_{NCO}$ to an infinite concentration of the reactive groups (i.e. $c^{-1} = 0$, see *Figure 1*), a value of $(1/r^c_{NCO})_e$ of 2.1 was found, which is higher than expected (i.e. 2, from equation (3)). There are three possible explanations for this higher value: (i) the supposition that the functionality of TI ($f_{w,TI}$) is 3.1 (and $f_{w,PD}$ is 2), or PD ($f_{w,PD}$) is 2.05 (and $f_{w,TI}$ is 3); (ii) the existence of a positive substitution effect in PD (a possible substitution effect in TI does not change the extrapolated value of $(1/r^c_{NCO})_e$ in the presence of excess hydroxyl groups) and; (iii) the supposition that a part of the PD molecules bear more reactive (i.e. primary) hydroxyl groups.

Suggestion (i) is not likely because experimentally determined NCO (TI) and OH (PD) concentrations correspond to values of $f_{w,TI}$ and $f_{w,PD}$ of 3 and 2, respectively. Suggestion (ii) can also be excluded, on account of the length of the PD molecule. The most probable reason seems to be suggestion (iii). A modification of the theory of branching processes for TI and PD, in which PD was considered as a mixture of molecules bearing both secondary and primary OH groups, showed that ≈4% of PD molecules in which both of the hydroxyl groups are primary is sufficient for obtaining the extrapolated value of $(1/r^c_{NCO})_e$ of 2.1. The modification of the theory was similar to that previously used for three-component polyurethane systems[2]. It was also found that the value of 4% is practically independent of the ratio of the rate constants of the primary (k_1) to the secondary (k_2) hydroxyl group in the region where $k_1/k_2 > 10$.

The number-average molecular weight

The dependence of the corrected experimental molecular weights, $\bar{M}_{ne}$, of blocked samples on the measured experimental conversions of the NCO groups, p_{NCO}, for both ratios of reactive groups, r_{NCO} (i.e. 1.0 and 0.8) are given in *Figure 2*. The theoretical (ring-free) molecular weights, $\bar{M}_n$, for given p_{NCO} values, calculated from equation (3) are also included; these latter values

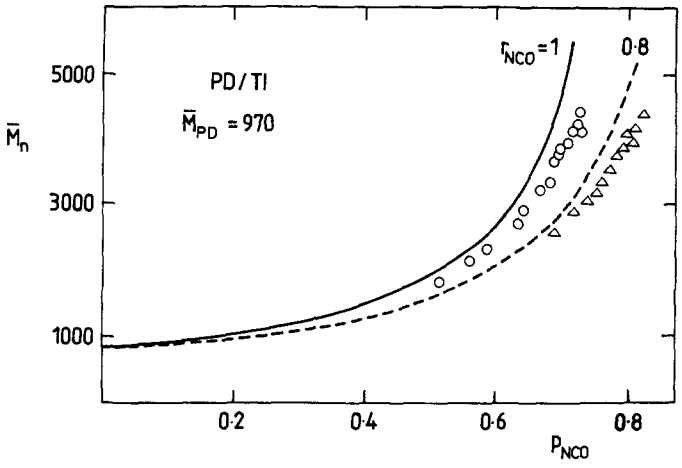

Figure 2 Dependence of the number-average molecular weight, $\bar{M}_n$, on the conversion of the NCO group, p_{NCO}, in the PD/TI system: ○, experimental values ($r_{NCO}=1$); ——, theoretical values ($r_{NCO}=1$); △, experimental values ($r_{NCO}=0.8$) and; – – –, theoretical values ($r_{NCO}=0.8$)

do not depend on the reactivity of the OH groups in PD. As can be seen, the theoretical $\bar{M}_n$ values are always higher than the experimental ones, as a result of cyclization.

The amount of groups that are wasted in the formation of intramolecular cycles can be expressed as the difference in the conversion values of the real and the ring-free processes that are needed to reach a given experimental molecular weight, $\bar{M}_{ne}$, i.e.

$$\Delta p = p_{NCO} - p_{NCO}(rf) \tag{8}$$

where the theoretical value has been calculated from equation (3); this can be rearranged to give:

$$p_{NCO}(rf) = [(2r_{NCO}+3)\bar{M}_{ne} - 2r_{NCO}M_{TI} - 3\bar{M}_{PD}]/6r_{NCO}\bar{M}_{ne} \tag{9}$$

The relative intramolecular conversions, s, defined by

$$s = \Delta p/p_{NCO} \tag{10}$$

were also calculated, together with the number of ring structures per single molecule in the system, N_r, which according to Stepto[4] is given by

$$N_r = 1 - \frac{[1+f_{n,TI}/(f_{n,PD}r_{NCO}) - f_{n,TI}p_{NCO}]\bar{M}_{ne}}{M_{TI}+f_{n,TI}\bar{M}_{PD}/f_{n,PD}r_{NCO}} \tag{11}$$

The dependences of both cyclization parameters, s and N_r, on the conversion p_{NCO} are given in *Figure 3*. The fraction of bonds wasted in cycle formation (s) increases with the conversion for both ratios of r_{NCO} (1.0 and 0.8), and near the gel point has values of ≈ 0.04 and ≈ 0.6, for $r_{NCO}=1.0$ and 0.8, respectively. The fraction of intramolecular structures, N_r, also increases with conversion and close to the gel point it reaches values of ≈ 0.28 and ≈ 0.20, for $r_{NCO}=1.0$ and 0.8, respectively.

The extent of cyclization from gel point conversions

In addition to measurements of the molecular weight, the extent of cyclization can also be characterized by a shift of the critical gel point conversion, p^c_{NCO}, or the critical molar ratio r^c_{NCO}. Since both methods yield values of Δp, the values of s can be compared. If the probability exists that a bond (which can be either inter- or intramolecular) is not correlated with the status of other bonds then the conversion of groups to intermolecular bonds, p_{inter}, is simply given by

$$p_{inter} = p(1-s) \tag{12}$$

where s is the fraction of bonds wasted in cycles and p is the overall conversion.

For the random case, using equation (1), we obtain (with $s = s_{OH} = s_{NCO}$)

$$p^c_{OH}p^c_{NCO}(1-s)^2 = [(f_{w,PD}-1)(f_{w,TI}-1)]^{-1} = X^* \tag{13}$$

whereas for the ring-free case (denoted by the subscript rf)

$$(p^c_{OH}p^c_{NCO})_{rf} = X \tag{14}$$

It can be seen from equation (12) that

$$\Delta p^c/p^c = [p^c_Y - (p^c_Y)_{rf}]/p^c_Y = s(Y = OH, NCO) \tag{15}$$

For $r^c_{OH} = 1/r^c_{NCO}$, we find:

$$p_{NCO}=1;\ (p_{NCO})_{rf} = 1-s;$$
$$(r^c_{OH})_{rf} = r^c_{OH}(1-s)^2 \text{ and; } r^c_{OH}(1-s)^2 = X \tag{16}$$

from which the following relationships can be derived:

$$\frac{\Delta r^c_{OH}}{r^c_{OH}} = \frac{r^c_{OH} - (r^c_{OH})_{rf}}{r^c_{OH}} = s(2-s) \tag{17}$$

or

$$s = 1 - (1 - \Delta r^c_{OH}/r^c_{OH})^{1/2} \tag{18}$$

The values of $\Delta p^c/p^c$ and $\Delta r^c_{OH}/r^c_{OH}$ are not equal, as can be seen from the difference between equations (15) and (17).

However, the situation is more complicated because the groups that have reacted intermolecularly and intramolecularly cannot be distributed at random in the PD and TI units[5]. Among the states of the units only

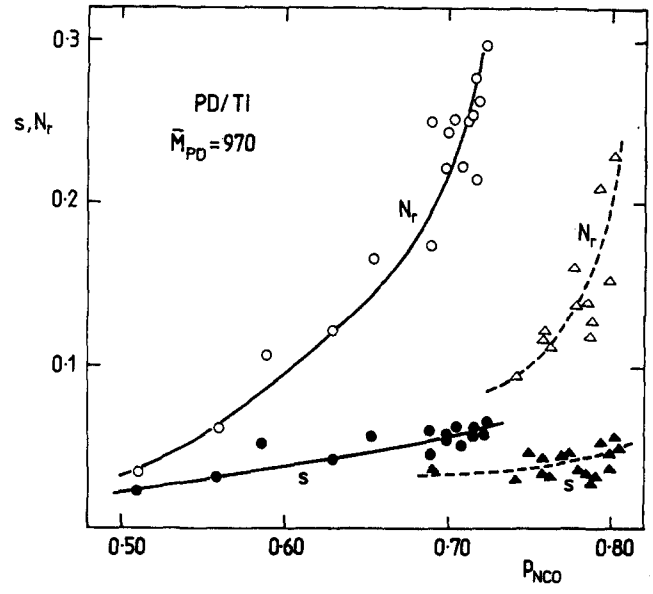

Figure 3 Dependence of the fraction of intramolecular bonds, s, and the fraction of intramolecular structures, N_r, on the conversion of the NCO group, p_{NCO}, in the PD/TI system: ○, N_r ($r_{NCO}=1$); ●, s ($r_{NCO}=1$); △, N_r ($r_{NCO}=0.8$) and; ▲, s ($r_{NCO}=0.8$)

* A similar equation for the reaction of f- and bifunctional monomers was derived earlier[13]

Table 1 Dependence on dilution of the critical molar ratio (r^c_{NCO}) and the fraction of intramolecular bonds (Δr^c_{NCO}) at the gel points (v^0 is the initial volume fraction of the PD and TI components)

v^0	1.0	0.37	0.23	0.17
$1/r^c_{NCO}$	1.98	1.75	1.60	1.45
Δr^c_{NCO}	0.057	0.167	0.238	0.310

Table 2 Experimental and theoretical values of $\Delta p^c/p^c$ and $\Delta r^c_A/r^c_A$

		Calculated[a]			
		RD theory		CD theory	
Quantity	Experimental	S_1	S_2	S_1	S_2
$\Delta p^c/p^c$ [b]	0.023	0.050	0.020	0.045	0.019
$\Delta p^c/p^c$ [c]	0.026	0.050	0.020	0.071	0.021
$\Delta r^c_{OH}/r^c_{OH}$	0.057	0.097	0.040	0.130	0.062

[a] Input parameters: $S_1 = 0.050$; $S_2 = 0.020$
[b] Initial molar ratio (r_{NCO}) = 1.0
[c] Initial molar ratio (r_{NCO}) = 0.8

those are realistic that have at least one group that has reacted intermolecularly. Thus, if the fractions of the units PD and TI, with i groups reacted intermolecularly and j groups reacted intramolecularly, are designated by a_{ij} ($i+j=0$–2) and b_{ij} ($i+j=0$–3), respectively, then only a_{00}, a_{10}, a_{11} and a_{20}, and b_{00}, b_{10}, b_{11}, b_{20}, b_{12}, b_{21} and b_{30}, may have a non-zero value, whereas a_{01}, a_{02}, b_{01}, b_{02} and b_{03} are all equal to zero in the random modification.

This problem had been reported earlier[5] and is discussed in more detail in the Appendix. There, a simple theory is presented which takes into account the constraints discussed above. In *Table 2*, the results of calculations of $\Delta p^c/p^c$ and $\Delta r^c_{OH}/r^c_{OH}$, using both the random distribution (RD) approach (see equations (11)–(17)) and the constrained distribution (CD) approach (theory given in the Appendix), are shown. Values of s (0.02 and 0.05), close to those obtained from $\bar{M}_n$ calculations, have been used as input parameters. The average value of s near to the gel point is close to 0.06 for $r_{NCO}=1$, and to 0.04 for $r_{NCO}=0.8$. However, none of the values of $\Delta p^c/p^c$ calculated by either theory are compatible with this value. A value of $s \approx 0.020$–0.025 gives a much better agreement, with the constrained model giving a somewhat better agreement than the unconstrained one.

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APPENDIX

An approximate theoretical treatment of the effect of cyclization on the gel point

In a monomer unit that cannot cyclize itself, at least one bond by which a neighbouring unit is bound must be intermolecular, while the other bonds can be either inter- or intramolecular. With this provision, let us assume that the probability for any additional bonds emanating from a unit to be either inter- or intramolecular is not correlated with the status (i.e. inter- or intramolecular) of the other bonds. In other words, the inter- and intramolecular bonds emanating from a unit associated with i bonds are distributed at random among the available $i-1$ bonds (one bond must be intermolecular). This distribution is controlled by a single set of cyclization parameters, s'_A and s'_B in this case, which are equal to the fractions of bonds used to close the cycles, and emanating from the components A and B, respectively, they are related to all of the existing $i-1$ bonds resulting from these units.

This assumption is a simplification when compared to a more exact model[5] in which the distribution of units, with respect to the number of inter- and intramolecular bonds, was calculated by the solution of sets of differential equations in which ring formation was taken into account. However, a comparison of numerical results has shown that, provided the above condition of at least one intermolecular bond is met, the deviations in the gel point conversion from the more precise model[5], at least for a low extent of cyclization, are not serious. The exact model gives a somewhat narrower distribution, i.e. a lower fraction of trifunctional units with two ring-closing bonds, but at these levels of cyclization ($s=0.02$–0.05) this fraction is almost negligible, anyway. The derivation given below is a modification of an approach based on the theory of branching processes, and has been used before for the analysis of network formation in polyurethanes[2,5,12]. For the case of a bifunctional (A) and a trifunctional (B) monomer, the probability generating function for the number fractions of intermolecular bonds emanating from a building unit, F_{0n}, is obtained by modification with a cyclization parameter τ:

$$F_{0n}(z) = n_A(a_0 + a_1 z_B + a_2 z_B^2 \tau_A) + n_B(b_0 + b_1 z_A + b_2 z_A^2 \tau_B + b_3 z_A^3 \tau_B^2) \quad \text{(A1)}$$

where a_i and b_i are the fractions of units giving i bonds and z is a variable of the probability generating function (p.g.f.) where the subscript denotes the direction of the bond looking out of the unit in question; n_A and n_B are the molar fractions of components A and B, respectively.

The parameters τ_A and τ_B have the following form:

$$\tau_A = 1 - s'_A + s'_A z_B^{-1} \quad \text{(A2)}$$

and

$$\tau_B = 1 - s'_B + s'_B z_A^{-1} \quad \text{(A3)}$$

where s' is the cyclization probability defined above. Inclusion of the z^{-1} factors reflect the fact that an intramolecular bond is not active in branching and is thus not counted in F_{0n}, i.e. the power of z is decreased by 1.

The procedure which follows is a standard one. The p.g.f. for the number of bonds resulting from units already bound by one of its bonds is obtained by differentiation with respect to z_A or z_B and normalization to unity:

$$F_A(z_B) = [a_1 + 2a_2(1 - s'_A)z_B + a_2 s'_A]/[a_1 + a_2(2 - s'_A)] \quad \text{(A4)}$$

and

$$F_B(z_A) = [b_1 + 2b_2(1 - s'_B)z_A + b_2 s'_B + 3b_3 z_A^2 \tau_B^2 - 2b_3 s'_B z_A^3 \tau_B] / [b_1 + b_2(2 - s'_B) + b_3(3 - 2s'_B)] \quad \text{(A5)}$$

The gel point condition is defined by the equation

$$F_A^B F_B^A = 1 \quad \text{(A6)}$$

where F_X^Y are the following derivatives:

$$F_X^Y = [\delta F_X(z)/\delta z_Y]_{z=1} \quad \text{(A7)}$$

From equations (A4) and (A5), we obtain the following:

$$F_A^B = [2a_2(1 - s'_A)]/[a_1 + a_2(2 - s'_A)] \quad \text{(A8)}$$

and

$$F_B^A = [2b_2(1 - s'_B) + 2b_3(3 - 4s'_B) + 2b_3 s'^2_B] / [b_1 + b_2(2 - s'_B) + b_3(3 - 2s'_B)] \quad \text{(A9)}$$

For the random case, the coefficients a_i and b_i are coefficients of the binomial expansion of probabilities that a bond has or has not reacted, which is given by the conversion of the reactive groups, p_A and p_B, i.e.

$$a_1 = 2p_A(1 - p_A) \quad \text{(A10)}$$

$$a_2 = p_A^2 \quad \text{(A11)}$$

$$b_1 = 3p_B(1 - p_B)^2 \quad \text{(A12)}$$

$$b_2 = 3p_B^2(1 - p_B) \quad \text{(A13)}$$

$$b_3 = p_B^3 \quad \text{(A14)}$$

Using these relationships, the parameters of the gel point condition (see equation (A6)) are as follows:

$$F_A^B = [2p_A(1 - s'_A)]/[2 - p_A s'_A] \quad \text{(A15)}$$

$$F_B^A = [2p_B(3 - 4p_B s'_B + p_B s'_B)]/[3 - p_B s'_B(3 + 2p_B s'_B)] \quad \text{(A16)}$$

From equation (A6) plus equations (A15) and (A16), the critical conversions at the gel point can be calculated, bearing in mind that $p_A = r_B p_B$, and $r_B = [B]_0/[A]_0$. The critical molar ratio, r_{Ac}, can also be calculated by making the following substitutions: $p_A = r_B$ and $p_B = 1$ (minority groups). Thus, the input information still required is the cyclization probabilities s'. As shown above, s' is not related to all of the bonds but only to specific ones. However, the s values that are obtained from M_n are related to all of the formed bonds. In terms of the coefficients a_i and b_i, these relationships read

$$s_A = a_2 s'_A/(a_1 + 2a_2) = s'_A(2/p_B) \quad \text{(A17)}$$

and

$$s_B = [b_2 s'_B + b_3 2s'_B(1 - s'_B) + 2b_3 s'^2_B]/(b_1 + 2b_2 + 3b_3) = s'_B p_B(3 - p_B)/3 \quad \text{(A18)}$$

If one wants to calculate the gel point conditions from the values of s, equations (A17) and (A18) can be used for transformation of s into s':

$$s'_A = s_A(2/p_A) \quad \text{(A19)}$$

and

$$s'_B = 3s_B/[p_B(3 - p_B)] \quad \text{(A20)}$$

or for r_B^s:

$$s'_A = s_A(2/r_B^s) \quad \text{(A21)}$$

and

$$s'_B = 3s_B/2 \quad \text{(A22)}$$

For alternating (A + B) reactions, the number of reacted A groups must be equal to the number of reacted B groups, namely

$$2n_A p_A = 3n_B p_B \quad \text{(A23)}$$

and so must be equal to the numbers of inter- and intramolecular bonds, respectively, i.e.

$$2n_A p_A s_A = 3n_B p_B s_B \quad \text{(A24)}$$

from which it follows that $s_A = s_B$. This equality, however, does not apply to s'_A and s'_B, which is evident from the equations (A17)–(A19).

With respect to the main body of the article, $p_A \equiv p_{OH}$ and $p_B \equiv p_{NCO}$.