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Formation of Polyurethane Networks Studied by the Gel Point Method

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SUMMARY

Determination of critical stoichiometric ratio necessary for gelation in polyurethane systems composed of poly(oxypropylene)triol and diol, trimethylolpropane and 4,4'-diphenylmethane diisocyanate revealed the effects of a different functionality, reactivity of functional groups, tendency to cyclization and the course of the crosslinking process.

INTRODUCTION

The critical conversion at gelation reflects the effect of functionality of the building components and laws of making bonds including the reactivity of functional groups, and is also affected by cyclization. In the case of alternating polyaddition reaction with equireactive functional groups corresponding to the formation of polyurethane networks from polyols and polyisocyanates, the gel point condition in the absence of cyclization is given by the expression (STOCKMAYER 1952)

$$[(\xi_{OH})_c(\xi_{NCO})_c]^{-1} = (f_{OH}-1)(f_{NCO}-1) \qquad (1)$$

where f_{OH} and f_{NCO} are functionalities of the polyol and isocyanate and $(\xi_{OH})_c$, $(\xi_{NCO})_c$ are critical conversions of OH and NCO groups, respectively. For components polydisperse in functionality f_X is the "weight" average: $f_X = \sum f_X^2 n_{Xf}/\sum f_X n_{Xf}$, where n_{Xf} is the molar fraction of the X component bearing f functional groups.

The differences in reactivity of functional groups and the cyclization introduce complications in the treatment of network formation. The effect of cyclization is treated by several perturbation methods of the tree-like model (KILB 1958, FRISCH 1955, GORDON SCANTLEBURY 1968), but an exact theory is not available due to long-range correlations in the structure arising from ring formation. The perturbation treatments are all based on the conformational statistics (usually Gaussian) of a single path connecting the functionalities and neglect any effect of the existing cycles

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and volume exclusion on positional probabilities of a pair of reacting groups. The relative tendency to cyclization with respect to the intermolecular reaction depends on the parameter Λ

$$\Lambda = B/C \qquad B = (3/2\pi\nu b^2)^{3/2} \tag{2}$$

where ν is the number of bonds in the smallest ring, b is the effective bond length and C is the molar concentration of functional groups. The ring-closure probability which depends on the chain flexibility (b) and on the size of the smallest cycle ν, is obtained by summation of B over cycles of all possible sizes. One of the simplest treatment due to KILB (1958) assumed cyclization along a single unbranched path only. STEPTO (1974) and AHMAD et al. (1978) improved this approach by considering additionally the ring closures involving unreacted functionalities of multifunctional units and units adjoining them. The theory of branching processes (TBP) (DUŠEK, VOJTA 1977) takes into account the whole complexity of the existing structures which are conversion dependent.

The effect of differences in reactivity can be treated by TBP (GORDON, SCANTLEBURY 1964); usually only the first shell substition effect is operative (reactivity of the given functional group depends only on the state of the groups within the building unit).

In this contribution the effects of cyclization, of differences in reactivities of functional groups and of the course of the crosslinking process on the formation of polyurethane networks have been studied using the critical molar ratio method (CRM). CRM is experimentaly feasible and consists in finding such ratio $r_c = [\mathrm{NCO}]_o/[\mathrm{OH}]_o = (\xi_{\mathrm{OH}})_c/(\xi_{\mathrm{NCO}})_c$ (with OH groups in excess), at which gelation occurs when the conversion of minority groups (NCO) approaches 100% $((\ \mathrm{NCO})_c = 1)$; then $(\xi_{\mathrm{OH}})_c = r_c$. $[\mathrm{NCO}]_o$ and $[\mathrm{OH}]_o$ are initial molar concentrations of functional groups. For an ideal case Eq.(1) yields

$$r_c^{-1} = (f_{\mathrm{OH}}-1)(f_{\mathrm{NCO}}-1) \tag{3}$$

EXPERIMENTAL

Material

Poly(oxypropylene)triols (PPT) and diol (PPD) (Niax Polyol, Union Carbide) were dried by azeotropic distillation with benzene. The number-average molecular weight (M_n) and functionality (f_n) of poly(oxypropylene) polyols were as follows:

		M_n	f_n
poly(oxypropylene)triol	LHT 240	710	2.89
	LG 56	2630	2.78
poly(oxypropylene)diol	PPG 1025	930	1.94

M_n values were determined by GPC; f_n was calculated using M_n values and the content of OH groups in the polyol.

Trimethylolpropane (TMP) and 4,4´-diphenylmethane diisocyanate (MDI) were distilled at 426 K/400 Pa and 448 K/270 Pa, respectively. The content of functional groups in polyol and MDI was determined by titration. The NCO groups were determined using the reaction with dibutylamine (DBA) and content of OH groups was obtained by adding phenyl isocyanate in excess followed by determination of unreacted phenyl isocyanate with DBA.

Preparation of networks

Polyurethane networks from MDI and polyols were prepared both in bulk and in benzene solutions at 343 K with dibutyltin dilaurate catalyst (0.02-0.08%). The reaction processed 1-5 days in sealed ampoules under nitrogene. All samples were prepared with an excess of OH groups.

Determination of the critical molar ratio r_c

The value of r_c was determined by extraction of reacted samples and the critical ratio was taken between values of r for the last completely soluble and the first sample with some gel fraction.

RESULTS AND DISCUSSION

The following systems were studied:

(a) binary systems composed of the poly(oxypropylene) triol (PPT) and the diisocyanate (MDI). As the reactivities of OH groups are equal and independent, the system is suited for the study of cyclization;

(b) ternary systems composed of poly(oxypropylene)diol (PPD), a triol (either PPT or trimethylolpropane (TMP)) and MDI. The unequal reactivities of primary OH groups in TMP and secondary ones in PPD as well as a possible substitution effect in TMP will affect network formation. The system composed of PPT, PPD and MDI is a reference system with equireactive OH groups. The networks were prepared in one stage, or in two stages via the MDI-PPD prepolymer.

(a) Binary systems

As expected, cyclization increases with increasing dilution and decreasing molecular weight of PPT. The system with the shorter triol LHT 240 is characterized by a greater slope of the plot r_c^{-1} vs. C^{-1} in Fig.1, which is a measure of the tendency to cyclization, but the dependence is more curved than predicted by TBP (Kilb´s and Stepto´s theories predict a linear dependence). The theories are either too approximate or an effect of the solvent nature on cyclization is operative. Theoretical curves were calculated for monodisperse triols f=3 and shifted to the experimental point corresponding to the reaction in bulk.

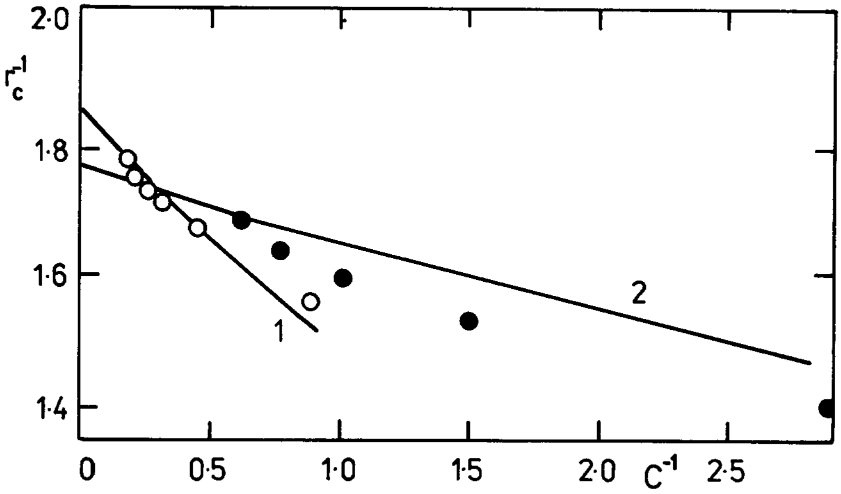

Fig. 1 The dependence of the critical ratio on dilution for MDI-PPT networks

○ LHT 240-MDI, ● LG 56-MDI, —— theoretical curves calculated from TBP - 1 LHT 240-MDI, 2 LG 56-MDI

For a constant effective bond length b the Kilb´s theory predicts the ratio of slopes of the dependences in Fig.1 to be $\beta_{LHT}/\beta_{LG} = (\nu_{LG}/\nu_{LHT})^{3/2} = 4.9$ (cf. Eq.(2)), but the experimental value is 2.8. This difference is caused by a change in b, which is a chain flexibility parameter (cf. Eq.(2)). The network chains are composed of a flexible part of polyoxypropylene and a stiff one of MDI and urethane units; therefore the system with longer PPT (LG 56-MDI) is more flexible resulting in a smaller b vaule. Values of b calculated according to Kilb´s and Stepto´s theories are given in Table 1.

TABLE 1
Values of the effective bond length b in nm

	Kilb		Stepto	
	b_o	b_c	b_o	b_c
LHT 240	0.28	0.43	0.27	0.41
LG 56	0.20	0.33	0.20	0.32

b_o and b_c values were determined using initial and critical concentration of functional groups, respectively.

For linear polyoxypropylene the value of b is 0.34 nm; therefore b_c values are more probable (cf. Table 1), since the majority of the cycles are formed in the vicinity of the gel point.

By non-linear extrapolation of the dependence r_c^{-1} vs. C^{-1} the cyclization is eliminated and the determination of weight-average functionality of the polyol f_w (FOGIEL 1969) using the relation

$$f_w = 1 + (r_c^{-1})_{C^{-1}\to 0} \qquad (4)$$

as well as the polydispersity in functionality (f_w/f_n) is possible. For poly(oxypropylene)triols the following results were obtained

	f_w	f_n	f_w/f_n
LHT 240	2.92	2.89	1.01
LG 56	2.90	2.78	1.04

f_w was determined with an error ± 2.5%.

(b) Ternary systems

Unequal reactivity. The systems PPD-PPT-MDI (system A) and PPD-TMP-MDI (system B) both contain a trifunctional (crosslinking) agent besides the bifunctional diol, but the triols differ in reactivities of OH groups. Whereas in system A all OH groups are equireactive, TMP in system B bears more reactive primary OH groups than are the secondary ones in PPD.

The difference in reactivity affects the gel point (Fig.2) by lowering r_c in comparison with the equireactive system A. In the two-stage procedure, the effect of unequal reactivity disapprears. The experimental data (Fig.2) do not give any evidence of the possible substitution effect in TMP.

Cyclization. Both systems A and B differ in the tendency to cyclization which also depends on the type of the crosslinking process. In the system A (PPD-PPT-MDI) the degree of cyclization, characterized by the slope of curves in Fig.3, is almost independent of the network formation process. However, in the one-stage process applied to the system B cyclization is very weak (Fig.3).

This fact can be explained by the formation of stiff clusters of TMP-MDI units in system B where cyclization is not likely due to chain stiffness. Clustering is enhanced by the unequal reactivity of TMP and PPD and is affected by the type of the crosslinking process. Clusters are preferably formed in the one-stage procedure (DUŠEK and ILAVSKÝ 1978), but in the two-stage process the difference in reactivity of OH groups in TMP and PPD does not play any role (secondary OH groups of PPD were exhausted in the first stage), so that the amount of clusters is expected to be lower (DUŠEK and ILAVSKÝ 1978), the structure more flexible and cyclization stronger.

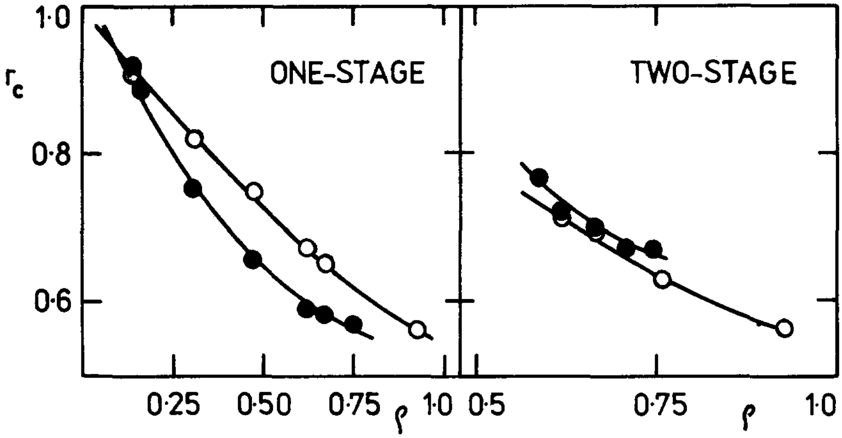

Fig. 2 Dependence of the critical ratio on the content of the triol ρ in one-stage and two-stage process of network formation, $\rho = (OH)_{triol}/(OH)_{tot}$

○ system A (PPD-PPT-MDI), ● system B (PPD-TMP-MDI)

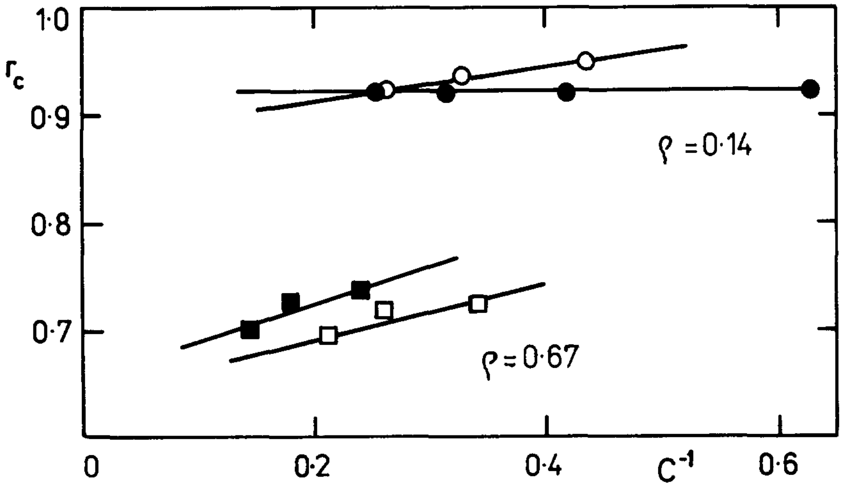

Fig. 3 Dependence of the critical ratio on dilution for networks of ternary system

○ □ system A (PPD-PPT-MDI),● ■ system B (PPD-TMP-MDI) in one-stage and two-stage process, respectively.

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