Rheological changes for urethane polymerizations in bulk and in solution

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Viscosity rise and extent of reaction were followed during the step growth polymerization of linear and branched urethanes in bulk and in solution. Results indicate that intra-molecular reaction may exist in both linear and branched systems. Adding solvent increases the extent of intra-molecular reaction. The system viscosity was found to correlate with CgM_w, where C is polymer concentration, g is the ratio of branched to linear polymer radii of gyration, and M_w is the weight-average molecular weight.

(Keywords: urethane polymerization; viscosity rise; gelation; intra-molecular reaction; linear and branched systems; solution polymerization; bulk polymerization)

INTRODUCTION

For a polymer melt, the zero shear rate viscosity is usually expressed as a function of a friction factor and a structure factor. If the polymer is linear,

$$\eta_0 = KM_w^a \qquad (1)$$

where K is a temperature dependent friction factor and the weight-average molecular weight, M_w, is the structure factor.

A linear dependence of viscosity on the weight-average molecular weight was found for polydispersed systems at low molecular weights[1]. At high molecular weights, chain entanglement is encountered, and the power of molecular weight dependence increases from 1.0 to 3.4. The value of a equals 3.4 if M_w is greater than a critical molecular weight, M_c, beyond which the effect of chain entanglement dominates the system viscosity. The value of a lies between 1.0 and 2.5 if M_w is less than M_c.[2]

For polymer solutions, the structure parameter, M_w, is modified by multiplication with the polymer concentration, i.e. CM_w.[3–6] The solvent can effectively decrease the extent of polymer–polymer interactions and delay the onset of chain entanglement to a higher molecular weight. The critical molecular weight for chain entanglement in the polymer solution is generally expressed as M_c/ϕ, where ϕ is the volume fraction of polymer in the solution with $\phi = C/\rho$. The frictional factor, K, is also a function of polymer concentration. Thus, for polymer solutions, the zero shear rate viscosity can be expressed as:

$$\eta_0 = K(C)(CM_w)^a \qquad (2)$$

Based on molecular theories, Bueche *et al.*[7,8] considered the chain entanglement effect in polymer solutions and theoretically derived the viscosity expression as follows:

$$\eta_0 = KC^4 \times M_w^{3.5} = KC^{0.5}(CM_w)^{3.5} \quad \text{for } M_w > M_c \quad (3)$$

Experimentally, Graessley *et al.*[5] found that, for polyisoprene in tetradecane with polymer concentrations ranging from 0.02 tp 0.33 g/ml, the zero shear rate viscosity could be expressed as:

$$\eta_0 = KC^5 \times M_w^{3.5} = KC^{1.5}(CM_w)^{3.5} \qquad (4)$$

The size of polymer molecules has a dominant effect on the viscosity change in a polymer solution. The solvent dilution and solvent thermodynamic effects on the viscosity come from the change in size of polymer coils under different environments[9,10].

For polymer systems with long branched chains, such as regular stars, regular combs and random trees, different viscosity dependencies on molecular weight were observed[5,11,12]. At low and intermediate concentrations, the viscosity of a branched polymer is less than that of a linear polymer with the same molecular weight due to the fact that the branched system has a smaller radius of gyration than that of the linear system. The ratio of the gyration radii can be expressed as $g = S_B^2/S_L^2$. Thus, $g \leqslant 1$ and decreases with increased branching. For branched polymers, the structure parameter is modified as gM_w. Physically the quantity gM_w is the weight-average molecular weight of a linear chain with the same radius of gyration as the branched chain. This approach has been used to describe the viscosity for branched polymers, such as polyisoprenes with star-branches[5,11], and polybutadiene[13].

In summary, the zero shear rate viscosity of a branched polymer system can generally be expressed as:

$$\eta_0 = KC^a(CgM_w) \qquad \text{if } M_w < M_c/\phi \qquad (5)$$

and

$$\eta_0 = KC^a(CgM_w)^b \qquad \text{if } M_c/\phi < M_w \qquad (6)$$

where a ranges from 0.5 to 1.5, and b equals 3.4. The effect of solvent concentration on the polymer size is not clear; usually, an empirical value of a is required for a given system.

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Equations (5) and (6) are mainly derived to describe the viscosity of non-reactive polymer systems at an equilibrium state. For a reactive system, the system viscosity increases with conversion. It is important to know whether the relationship derived for non-reactive systems at steady state can be employed to describe the dynamical reactive systems.

The rheological changes which occur during processing of thermoset polymers are enormous. Understanding these rheological changes can be critical to the processing of thermoset polymers. Roller[14] reviewed some recent studies regarding the rheology of curing thermoset polymers. In these studies, viscosity changes during processing are expressed as a function of time and temperature:

$$\eta = K\exp(E_v/RT)\exp(k(T)t) \qquad (7)$$

This model is useful for correlating experimental data measured at different temperatures. It, however, lacks kinetic justification and contains no fundamental information about the molecular structure.

The next level of modelling is to convert viscosity *versus* reaction time to viscosity *versus* conversion using independently measured kinetic data. A typical expression is[15–17]:

$$\eta = K\exp(E_v/RT)\left(\frac{\alpha_{gel}}{\alpha_{gel}-\alpha}\right)^{a+b\alpha} \qquad (8)$$

where α is polymer conversion and α_{gel} is the gel conversion. Such a correlation corrects for the effect of reaction rate due to various catalyst concentrations. The model, however, still does not incorporate any molecular structure.

From conversion data, the corresponding molecular weight can be calculated using appropriate theories. Thus, the viscosity changes during polymerization can be expressed as a function of weight-average molecular weight and an Arrhenius temperature dependence[18–21]:

$$\eta = K\exp(E_v/RT)[M_w/(M_w)_0]^{f(T,M_w)} \qquad (9)$$

This model brings the structure parameter, M_w, into the viscosity correlation. The function f, however, needs to be fitted empirically. For different systems, the maximum f values differed from 2.1–2.6 for an HDI-based polyurethane[18], 2.6 for poly(dimethyl siloxanes)[19], and 3.4–6.7 for a MDI-based polyurethane[20].

For crosslinkers with differing functionalities, the weight-average molecular weight does not correlate well with the viscosity data. Valles *et al.*[19] studied the viscosity changes during bulk reactions of poly(dimethyl siloxanes) with random branches. When plotting the viscosity *versus* weight-average molecular weight, the curves for branched systems do not follow that for the linear system. Instead, if the gyration effect is considered, the plots of η_0 vs. gM_w fall into a single curve for data taken from various branched systems. This result is similar to the star-branched polyisoprene system studied by Graessley[11].

In this work, the rheological changes of polyurethane reactions in an inert solvent (nitrobenzene) with different polymer contents are investigated. Materials studied include both linear and crosslinked polyurethanes.

EXPERIMENTAL

Experimental studies of both linear and branched polyurethane reactions were conducted. Different concentrations of polyurethane (PU) in nitrobenzene (NB) were used: bulk PU, 70% PU/NB, 50% PU/NB and 30% PU/NB by weight. The urethane reaction was based on either a polyester triol or a polyester diol (TONE-310 or TONE-210, Union Carbide) and a diisocyanate (MDI, 143-L, Dow Chemical). The diol, TONE-210, has an average molecular weight very close to that of the triol, TONE-310 (i.e. 830 vs. 900) and the diisocyanate has a molecular weight of 287. A list of stoichiometric ratios of these materials is given in *Table 1*. Dibutyltin dilaurate (T1 2) was used as the catalyst at a concentration of 24.3 ppm (by weight) in the diol system and 3.8 ppm in the triol system.

A Haake viscometer with model MVII was used to measure the system viscosity before gelation. The model MVII has a cup with an inside diameter of 42 mm, a rotor with an outside diameter of 36.8 mm and a length of 60 mm. Hot water was circulated in a heating jacket outside the measuring cup to control the system temperature at 60°C which was verified by occasionally inserting a thermocouple into the gap between the cup and the rotor during reaction. During polymerization, different shear rates, ranging from 3.27 to 176.3 s^{-1} were applied to the system by changing the gear to different slots. The system viscosity was measured every 40 s until the sharp rise in viscosity was observed and was continuously measured thereafter. Accuracy of the viscosity measurement depended on the sensitivity of the cable used in the Haake viscometer and also on the Weissenberg effect of the reacting polymers when reaching a higher viscosity. When the viscosity began rising sharply, material tended to climb the rotor, even at the lowest shear rate, due to the Weissenberg normal force effect. Consequently, the accuracy of any further viscosity measurement was severely reduced since the contact area between the material and the rotor was changed and the velocity profile in the gap was no longer an ideal Couette flow. The gel point is defined by extrapolating the viscosity rise curve to infinity.

For the kinetic study, a differential scanning calorimeter (Perkin–Elmer, DSC-2C) was used to measure the rate of heat released during polymerization. The calorimeter was set at 60°C, and one or two drops of mixture, weighing from 10–20 mg, were placed in a pre-weighed stainless steel pan. The pan was tightly sealed

Table 1 Materials used in urethane reactions

Polyurethane		Parts by weight
Resins	Triol (TONE 310, $f=3.0$)	67.21
	MDI (143L, $f=2.0$)	32.79
	Diol (TONE 210, $f=2.0$)	74.26
	MDI (143L, $f=2.0$)	25.74
Catalyst T-12		3.8 ppm in triol 24.3 ppm in diol
Solvent		Parts by weight
Nitrobenzene (NB)		PU-70/NB-30 PU-50/NB-50 PU-30/NB-70

and loaded into the calorimeter. The stainless steel pan is designed with an O-ring inside to prevent escape of any solvent or monomer that vapourizes during the experiment. Isothermal reactions were stopped when there was no further reaction heat released. Samples were then reheated from room temperature to 230°C in the scanning mode with a heating rate of 5°C/min to determine the residual exotherm left in the isothermally reacted samples. The total heat of reaction was calculated from the areas under both the isothermal and the scanning d.s.c. curves.

RESULTS AND DISCUSSION

The cross plots of viscosity changes *versus* polymer conversion for branched and linear systems are given in *Figures 1* and *2*, respectively. These curves indicate that solvent dilution has a great effect on viscosity rise. *Figure 1* also shows a delay of gel conversion due to the increase of solvent content in the branched systems.

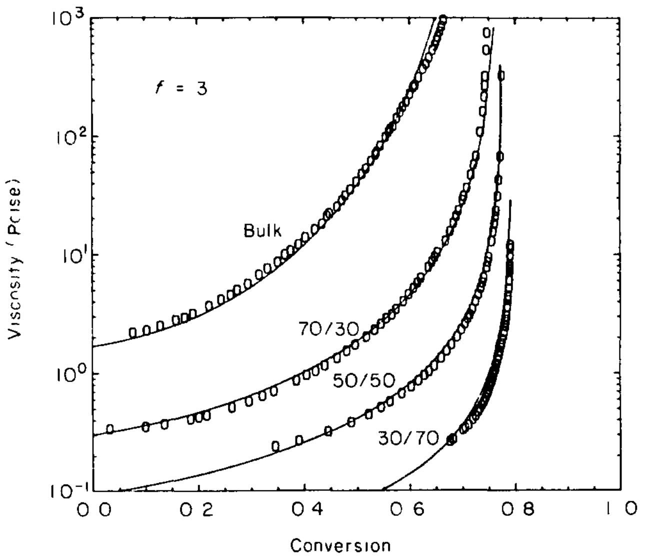

Figure 1 Viscosity *versus* PU conversion for systems with $f = 3$ at 60°C, (○) experimental results and model simulations, equation (12), (———)

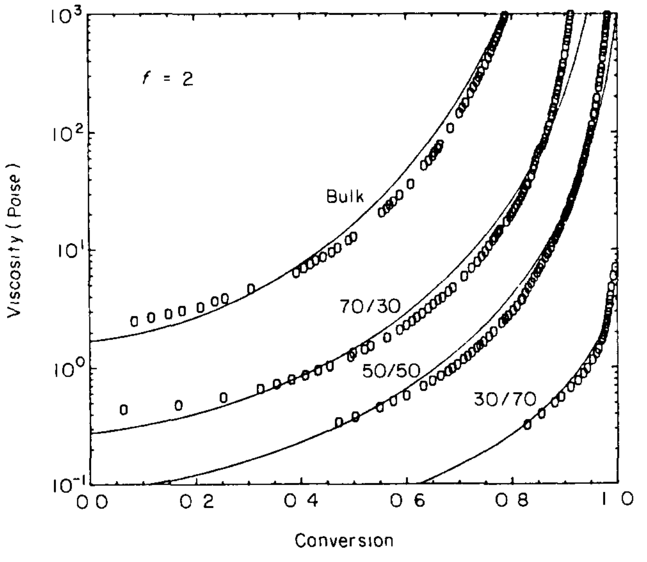

Figure 2 Viscosity *versus* PU conversion for systems with $f = 2$ at 60°C, (○) experimental results and model simulations, equation (12), (———)

Modelling of viscosity changes

For a reactive system, it is well known that molecular weight increases with polymer conversion. Using the recursive nature of the branching process, Macosko and Miller[22] have developed the following expression for weight-average molecular weight in a step growth copolymerization between a reactant of functionality f, A_f, and a comonomer of functionality 2, B_2:

$$M_w = w_{A_f}\left(M_{A_f} + \frac{f\alpha(M_{B_2} + r\alpha M_{A_f})}{1 - r\alpha^2(f-1)}\right) + w_{B_2}\left(M_{B_2} + \frac{2r\alpha(M_{A_f} + \alpha(f-1)M_{B_2})}{1 - r\alpha^2(f-1)}\right) \qquad (10)$$

M_{A_f} and M_{B_2} are the initial molecular weight of A_f and B_2, w_{A_f} and w_B are the weight fraction of A_f and B_2, respectively, r is the stoichiometric ratio, and α is polymer conversion.

For many reactive systems, the plots of relative viscosity *versus* polymer conversion form a single curve which is independent of reaction conditions. But in some other cases, such a correlation does not exist. This phenomenon has been discussed by several researchers[19,23–26]. These observations imply that an increase in molecular structure build-up may not necessarily be the same if the reaction conditions are varied. The reason for the difference is still unclear. It may be due to side reactions, ring formation or other factors. Some researchers consider the ring formation or intra-molecular reaction as the main reason for having different viscosity rises and gel conversions.

Experimental studies of intra-molecular reaction for linear and branched systems were conducted by Stepto *et al.*[24,25]. It is found that the extent of intra-molecular reaction increased when the reaction system was diluted by solvent, as indicated by the delay of gelation. Higher functionality of reactants, more flexible polymer chains, and larger molar mass of reactants also increased the extent of intra-molecular reaction and, consequently, resulted in a delay of gel formation.

In this paper, the intra-molecular reaction is considered in the calculation of molecular weight. Using Kilb's theory[27], the gel conversion, α_c, can be expressed as[28–30]:

$$P_c(f-1)(1-\lambda_{ab}) = 1 \qquad (11)$$

where

$$\lambda ab = C_{int}/(C_{ext} + C_{int})$$

and

$$P_c = \alpha_a \alpha_b$$

This expression uses a ring forming parameter, λ_{ab}, to account for the effect of intra-molecular reaction. This parameter is essentially the ratio of the probability of having the intra-molecular reaction, C_{int}, to the probability of having both inter-molecular and intra-molecular reactions. The existence of intra-molecular reaction delays the gel conversion as well as the growth of molecular weight. Such reaction should be considered in the viscosity modelling.

The viscosity and conversion data shown in *Figures 1* and *2* can be modelled by an equation similar to equation (9):

$$\eta = K_v(C)^a[M_{we}/(M_w)_0]^{b+c\alpha_e} \qquad (12)$$

where $(M_w)_0$ is the initial weight-average molecular weight. The effective molecular weight, M_{we}, is calculated from the polymer conversion with consideration of intra-molecular reaction. Here, we assume that only inter-molecular reactions contribute to the increase of molecular weight. The amount of conversion going to the inter-molecular reaction is designated as the effective conversion, α_e.

For non-linear polyurethane reactions, Standford and Stepto[25] showed that the plot of inter-molecular conversion *versus* total conversion forms a straight line. Thus, the effective conversion can be expressed as:

$$\alpha_e = (\alpha^0_{gel}/\alpha_{gel})\alpha_{tot} \qquad (13)$$

where α^0_{gel} is the calculated gel conversion without intra-molecular reaction, α_{gel} is the measured gel conversion and α_{tot} is the total conversion which includes both inter-molecular and intra-molecular reactions. The measured gel conversions, α_{gel}, are listed in *Table 2* for branched systems with different solvent contents.

For linear polyurethane systems, intra-molecular reaction was also detected experimentally by Stepto and Waywell[24], but the extent of intra-molecular reaction was much smaller than that of non-linear systems. Using the same approach for non-linear systems, the effective conversion for linear systems can be expressed as:

$$\alpha_e = (C_{ext}/C_{tot})\alpha_{tot} \qquad (14)$$

where

$$C_{ext}/C_{tot} = 1 - C_{int}/C_{tot} = 1 - \lambda_{ab} \qquad (15)$$

The parameter, C_{ext}/C_{tot} represents the probability of having inter-molecular reaction *versus* the probability of having any reaction and is very close to unity for linear systems. Here, assumed values of C_{ext}/C_{tot}, which give the best fit of the experimental data shown in *Figure 2*, are used to calculate the effective conversion in equation (14). Such values are listed in *Table 2* for linear systems with different solvent contents.

Table 2 Model parameters used in equation (12)

Branched systems							
PU/NB	C (g cm^{-3})	α_{gel}	K_v	a	b	c	f^*_{max}
Bulk PU	0.976	0.75	1.85	4	1	3.0	3.26
70/30	0.725	0.77	1.1	4	1	1.0	1.77
50/50	0.539	0.78	1.1	4	1	0.5	1.39
30/70	0.338	0.79	1.6	4	1	0.3	1.24
Linear systems							
PU/NB	C (g cm^{-3})	C_{ext}/C_{tot}	K_v	a	b	c	f^*_{max}
Bulk PU	0.976	1.00	1.85	4	1	3.0	4.00
70/30	0.725	0.99	1.0	4	1	1.7	2.68
50/50	0.539	0.97	1.0	4	1	1.4	2.36
30/70	0.338	0.95	1.6	4	1	0.6	1.57

* For branched systems, $f_{max} = b + c\alpha_{gel}$
For linear system, $f_{max} = b + c(C_{ext}/C_{tot})$

By knowing the effective conversion, α_e, the effective molecular weight, M_{we}, can be calculated from equation (10) for step growth polymerizations. The values of α_e and M_{we} can then be used in equation (12) to model the viscosity changes. The calculated values, as shown by the solid lines, for branched systems are given in *Figure 1*, and those for linear systems are given in *Figure 2*. A list of numerical values of K_v, a, b and c for all the systems studied here is given in *Table 2*. The value of a is maintained constant and equals 4.0 as suggested by equation (3). The value of b is set equal to 1.0 in order to predict a linear dependence of viscosity on molecular weight at low conversions. The correlated c value decreases as the solvent concentration increases. It is also found that the c values for linear systems are always greater than those of branched systems. This result indicates that, during polymerization, the viscosity of linear systems has a higher exponential dependence on molecular weight than that of branched systems.

The viscosity model based on equation (12) correlates very well with data for branched systems. However, for most linear systems, the calculated viscosities at high conversions are lower than the experimental results. If chain entanglement occurs during the period of viscosity rise, the value of $b + c\alpha_e$ in equation (12) should reach 3.4. For bulk polymerizations, both branched and linear systems apparently experience chain entanglement (i.e. $f_{max} = 3.26$ for the branched system and $f_{max} = 4.0$ for the linear system). The unreasonable high f_{max} value for the linear system may be due to the empirical nature of the model used. However, for solvent-diluted systems, the f_{max} values are quite low, especially for branched systems. The f_{max} value in *Table 2* ranges from 1.24 to 1.77 for branched systems and 1.57 to 2.68 for linear systems. This result seems to imply that, for diluted reaction systems, polymers formed remain unentangled before gel formation. However, this argument is found incorrect as discussed later.

Correlations between viscosity and structure parameters

Branched systems. For diluted systems, the polymer concentration, C, which is given in *Table 2* in units of g-PU cm^{-3} solution, must be included in the viscosity correlation. *Figure 3* is a log–log plot of viscosity *versus* CM_{we} for the branched systems. The results show that an increase in solvent content decreases the exponential dependence on molecular weight. This is consistent with the f_{max} values correlated from equation (12) (see *Table 2*). If we consider the gyration effect, a plot of viscosity *versus* CgM_{we} can be constructed as shown in *Figure 4*, where the radius of gyration ratio, g, is given by Zimm and Stockmayer[31], for $f = 3$:

$$g = \frac{3(1-2\alpha')}{\alpha'}\left[\frac{1}{2}\left(\frac{1-\alpha'}{\alpha'}\right)^{1/2} \times \ln\left(\frac{(1-\alpha')^{1/2}+(\alpha')^{1/2}}{(1-\alpha')^{1/2}-(\alpha')^{1/2}}\right) - 1\right] \qquad (16)$$

where f is the monomer functionality and α' is the Flory's branching probability and equals $r\alpha^2$, where α is polymer conversion and r is the stoichiometric ratio. Viscosity data for various diluted systems are brought into curves which are parallel to the curve of the bulk system. Such results indicate the existence of chain entanglement before gelation, even in the diluted systems, i.e. 30% PU/NB.

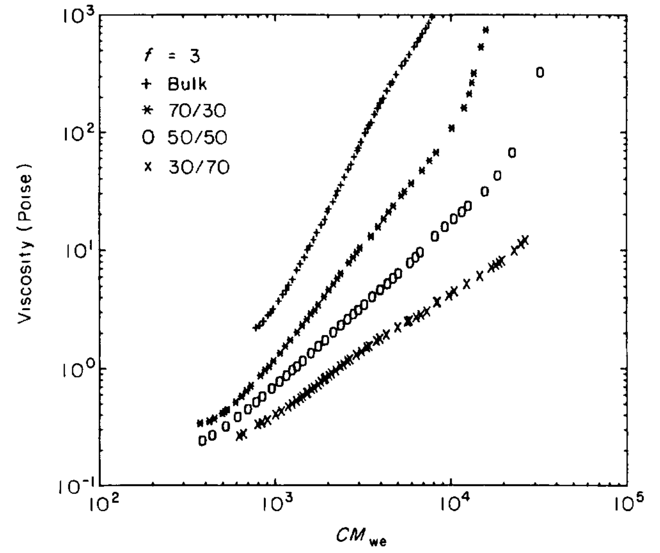

Figure 3 Viscosity *versus* CM_{we} for $f=3$ systems at 60°C

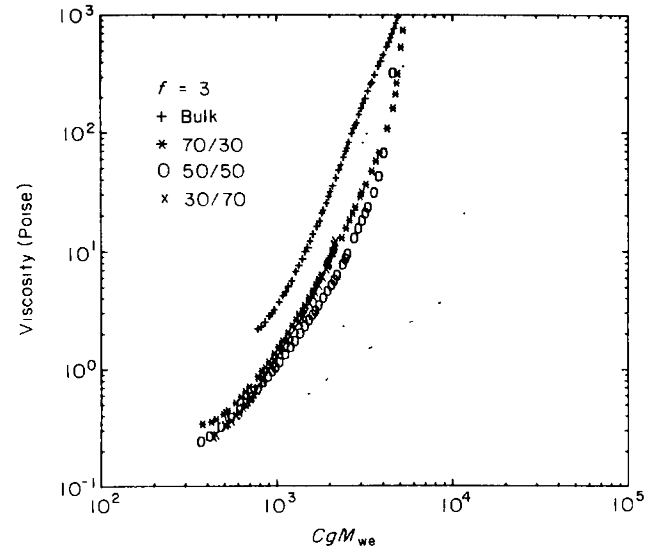

Figure 4 Viscosity *versus* CgM_{we} for $f=3$ systems at 60°C

Linear systems. For linear systems, the viscosity data can also be plotted *versus* the product of molecular weight and polymer concentration, as shown in *Figure 5*. Molecular weight, M_w, is calculated from total conversion by assuming no ring formation. When considering the intra-molecular reaction, the effective conversion and the effective molecular weight, M_{we}, are calculated from equations (14) and (10), respectively. A plot of viscosity *versus* CM_{we} for linear systems is given in *Figure 6*. The viscosity data for diluted systems are brought into lines parallel to that of the bulk system. The slope of these curves indicates the existence of polymer entanglement during reaction.

Finally, the curves for all the systems coincide when the viscosity data are divided by the friction factor, K_0, for each system, as shown in *Figure 7*. The value of K_0 for each system is given in *Table 3*, where K_0 for both bulk systems are set equal to unity. Using this plot, one can compare the slopes of the curves with the theoretical limits of 1.0 at low molecular weights and 3.4 at high molecular weights.

Intra-molecular reaction is found in both branched and linear systems, as indicated by the delay of gel formation and the values of C_{int}/C_{tot} given in *Table 3*. The extent of intra-molecular reaction *versus* total conversion, C_{int}/C_{tot}, can be calculated from the gel conversion for branched systems, equation (11), and from $1-C_{ext}/C_{tot}$ for linear systems. A plot of C_{int}/C_{tot} *versus* the inverse of polymer

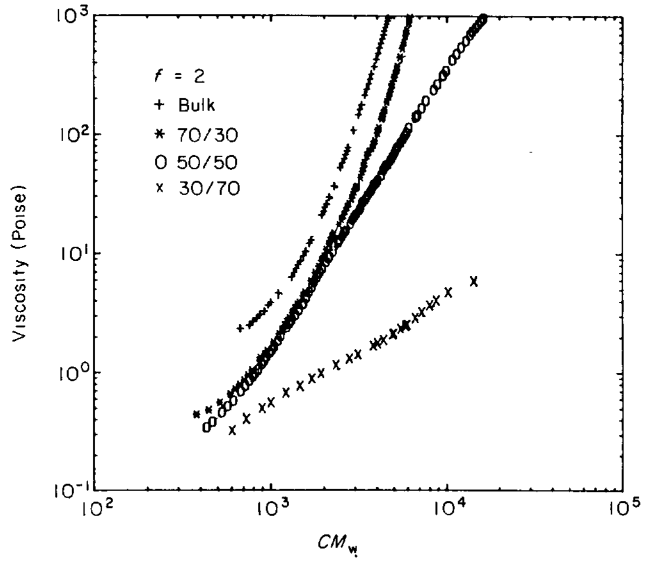

Figure 5 Viscosity *versus* CM_w for $f=2$ systems at 60°C

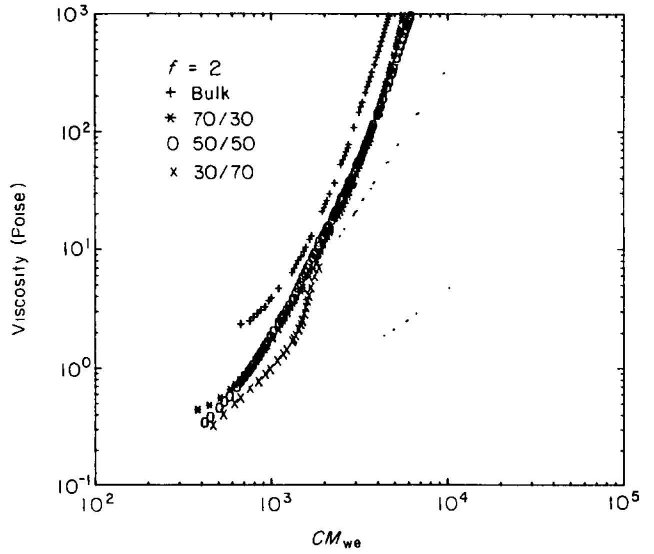

Figure 6 Viscosity *versus* CM_{we} for $f=2$ systems at 60°C

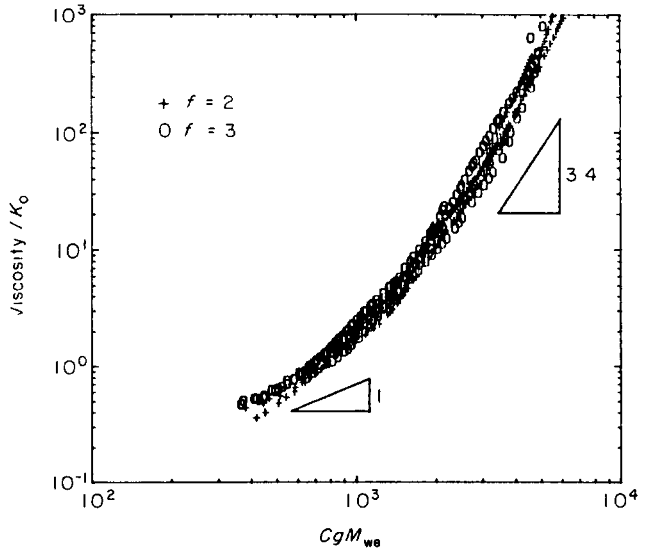

Figure 7 Viscosity/K_0 *versus* CgM_{we} for all the systems studied

Table 3 Friction factor and extent of intra-molecular reaction

	Branched		Linear	
PU/NB	K_0	C_{int}/C_{tot}	K_0	C_{int}/C_{tot}
Bulk PU	1.00	0.060	1.00	0.00
70/30	0.32	0.079	0.46	0.01
50/50	0.25	0.093	0.44	0.03
30/70	0.24	0.109	0.28	0.05

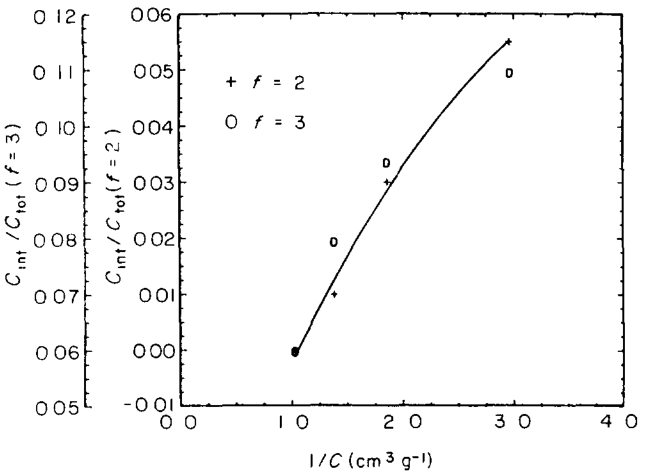

Figure 8 Extent of intra-molecular reaction, C_{int}/C_{tot}, *versus* inverse of polymer concentration, $1/C$, for all the systems studied

concentration is constructed for both branched and linear systems, as shown in *Figure 8*. The solid line is the least square fit of the data points by a second order polynomial equation. The values of C_{int}/C_{tot} for branched systems are always greater than those for linear systems due to the fact that branched systems have a higher possibility of forming ring structures.

Figure 8 shows that an increase of solvent concentration increases the extent of intra-molecular reaction which agrees with the results of other researchers[24-26,28-30]. It also indicates that the intra-molecular conversion for both systems has a similar dependence on solvent concentration.

CONCLUSIONS

Rheological studies of linear and branched polyurethane reactions in nitrobenzene with different solvent contents were conducted. The results provide useful information on the viscosity rise and structure build-up during polymerization. Viscosity data on both linear and branched molecules are brought together when plotted *versus* CgM_{we}, where C is polymer concentration, g is the ratio of polymer radii of gyration, and M_{we} is the weight-average molecular weight from the intra-molecular reaction. Viscosity curves indicate the existence of polymer chain entanglement during solution polymerization. These results also verify that the viscosity–molecular structure relationship derived for non-reactive polymer systems can be used in describing the structure build-up in reactive systems.

Direct measurement of the extent of intra-molecular reaction was not conducted in this study. However, the delay of gel conversion of urethane polymerization by increasing solvent content was observed. In the evaluation of ring formation based on the observation of the delay of viscosity rise and gelation, the dependency of extent of intra-molecular reaction on solvent content for both branched and linear systems are found to be quite similar. The extent of ring formation is very small during polymerization for linear systems; however, its effect on the viscosity rise is significant and cannot be neglected.

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