Correlation of Linear Viscoelastic Behavior and Molecular Weight Evolution in the Bulk Urethane Polymerization

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ABSTRACT: Bulk polymerization of urethane made from diphenylmethane 4, 4′ diisocyanate (MDI) and polyether macro diol was performed from size exclusion chromatography and viscoelastic studies. Coupling the viscoelastic characterization and the kinetic law showed that the viscoelastic behavior of the urethane system is only dependent of the degree of polymerization. The rheological study proved that low physical interactions can be found between the polyurethane chains. Furthermore, the critical molecular weight corresponding to a rheological maximum effect of these interactions was observed close to the value $Mc = 2Me$, characterizing the onset of the topological entanglement coupling. A qualitative explanation of this singular behavior was attempted from a hydrogen bonding point of view. On the other hand, the linear viscoelastic properties of polyurethane samples of different molecular weights were studied. The main viscoelastic parameters, η_0, J_e^0 and G_N^0 were determined. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2395–2406, 1997

Key words: viscoelasticity; polyurethane; kinetic; interactions

INTRODUCTION

In the formation of linear polyurethane elastomers, the reactants (diisocyanate and diol) join end to end to produce polymer chains linked together through urethane groups. Furthermore, due to the extensive diversification of possible constituents, a rather wide variety of mechanical properties can be obtained from these materials.

Although there is considerable published literature on the relation of polyurethane to their chemical and physical structures, much less has appeared concerning the detailed nature of urethane polymerization. Published detailed information on rheology of urethane polymerization, in particular the work of Macosko and co-workers,[1-3] mainly concerns thermoset urethane elastomer systems.

Therefore, the aim of the present work was to investigate bulk polymerization of urethane made from diphenylmethane-4, 4′ diisocyanate (MDI) and polyether macro diol. On the other hand, even though considerable interest in modeling viscosity increases during curing, little has been done on oscillatory rheological experiments. The oscillatory shear method has the advantage to measure *in situ* in the rheometer a continuous evolution of the linear viscoelastic properties, through the complex moduli G' and G'', of the reactive system. In addition to this rheological characterization, the extent of the polymerization reaction was measured as a function of time through the variation of molecular weights from size exclusion chromatography (SEC).

All these fundamental aspects must be well understood to approach the modeling of this reaction in a continuous reactor such as twin screw

extruder. Works are in progress with this purpose.

EXPERIMENTS

Experiments were performed on linear polyurethane system of 4, 4′ diphenyl methane diisocyanate (MDI, Desmodur 44M) and a polyether diol (M_n = 1 kg/mol, PU1600) of functionality 2. These products were generously supplied by Bayer Corporation. On the other hand, the urethane system was only made from soft segments because a chain extender was not added in the system for avoiding phase separation by hydrogen bond formation between hard segments.

Diol was preheated in a glass vessel at a temperature of 50°C under nitrogen. The stoichiometric concentration of MDI was stirred in the vessel and mechanical mixed with diol within 3 min. Without a catalyst, the rheological kinetic study ensured that the extent of the reaction at these conditions can be negligible.

As a catalyst, dibutyl tin dilaurate (DBTDL) was added in the system just before experiments in the rheometer.

Isothermal viscoelasticity experiments on catalyzed samples were done with the use of a Rheometrics RMS800 with parallel plate geometry of 50-mm diameter plates and a 1-mm gap. Then, the dynamic shear mode was used at the frequency of 1 rad/s. The reactive mixture was transferred, through a 2 mL syringe, to the parallel plate preheated at the experimental temperature. Complex shear modulus was recorded after approximately 10 s. On the other hand, strain amplitude was manual fitted from 800% at the beginning of the test to 1% at the end of the experiment to obtain a measurable torque and to remain in the domain of the linear viscoelasticity.

Viscoelasticity molecular weight correlations were also performed on a well-characterized nonreactive polyurethane system synthetized from the following procedure. Polyurethane samples were polymerized in a glass reactor at a temperature of 60°C with 1.34 × 10^{-4} mol/L of DBTDL. A solution of n-butylamine in tetrahydrofuranne (2% by weight) was injected in the reactor to quench the reaction. One day later THF was removed and samples were dried at 60°C for 3 days under vacuum at a reduce pressure. From this procedure, samples with different molecular weights were synthesized.

Table I   SEC and Rheological Kinetic Experiments of Bulk Urethane Polymerization

Temperature °C	[Cat] mols/L		
	1.34×10^{-4}	2.67×10^{-5}	8.9×10^{-6}
40	×		
60	×	×	
80	×	×	×
100	×	×	×
120			×

The molecular weights of the polymer samples were measured with a SEC system, which consisted of a Waters 510 pump, a Waters R410 refractometer, and two PSS linear columns (Mixed B) of 600 × 7.8 mm. Tetrahydrofurane (THF), at a flow of 1.2 mL/min, was used at room temperature as the solvent. The SEC was calibrated with polystyrene standard. Data were collected with a CNRS software (GPCHROM). To have comparative results between rheology kinetics and SEC kinetics, experiments were duplicated in the RMS, used in this case as a chemical reactor only. The sample products were collected from the two parallel plates through the sample port of the rheometer, directly into 8 mL vessels containing a solution of n-butylamine in THF (2% by weight) to quench the reaction.

Table I sums up the main polymerization experiments, rheology, and SEC kinetics carried out in this study. Three amounts of catalyst were used at three different temperatures in the range of 40 to 120°C.

RESULTS AND DISCUSSION

General Behavior

Figure 1(a−b) provides evidence of the urethane polymerization process through the variation of the complex modulus at ω = 1 rad/s (strorage G' and loss G'' moduli) and molecular weight, respectively. Such a behavior was observed at different temperatures of polymerization and at different amount of catalyst. The viscous behavior of the oligomeric material dominates the initial part of the experiment. The loss modulus G'' is large, while the storage modulus G' is still negligible. With increasing molecular weight, the loss modulus increases while the storage modulus rises

sharply until tan δ goes through a minimum value. However, the storage modulus does not intercept the loss modulus. Beyond this critical point, the loss modulus keeps increasing while the storage modulus increase slightly. Consequently, tan δ increases and reaches a maximum value. In the last part of the polymerization process, the storage and the loss moduli increase with reactional time and cross (tan $\delta = 1$ and $G' = G'' \approx 10^5$Pa). This crossover point between G' and G'' means that the onset of the plateau zone characterizing the presence of physical entanglements is reached at the experimental temperature ($T = 40°C$) and at the frequency $\omega = 1$ rad/s of the oscillatory shear applied.

On the other hand, Figure 1(b) shows that the average number molecular weight increases linearly with the reactional time as:

$$M_n/M_o = [Ao]kt + 1 \qquad (1)$$

where k is the kinetic constant and $[Ao] = 1.58$ mol/L is the initial concentration of diol (or diisocyanate) monomers. From a kinetics point of view, these experimental data behavior suggests that simplified assumptions can be made on the reaction mechanisms: (a) the mechanism of the reaction remains constant throughout the polymerization process; (b) the polymerization reaction is first order with respect to each functional group reactant, [H] and [NCO].

If we consider the isocyanate concentration equal to the active hydrogen [NCO] = [H], because the polymerization is run near stoichiometry, the simplest expression used to fit urethane kinetic data is, therefore:

$$-d[NCO]/dt = k[NCO]^2 \qquad (2)$$

Such a simplified kinetic expression was generally used for modeling the polymerization processing of the urethane system.[4–6] Last, from the combination of Carother's equation with the second-order rate expression, relation 1 is found.

SEC Kinetics

Remember that the molecular weight values were obtained from SEC and represent polystyrene equivalent molecular weights because the calibration curve of molecular weight vs. elution volume was established using a polystyrene standard.

A number of experiments, as previously described, were carried out to measure the kinetic constant. The temperature dependence was obtained by making measurements at three different temperatures ($T = 60$, 80, and 100°C) at the catalyst level of $[2.67 \times 10^{-5}$ mol/L]. Figure 2(a) and (b) show that M_n increases linearly with time. Then, eq. (1) is valid at different temperatures and at different catalyst concentrations. On the other hand, the kinetic constant k can be expressed as:

$$k = A1 \exp(-Ea/RT) \qquad (3)$$

where R is the gaz constant and Ea is the activation energy of the reaction. The activation energy was measured from the Arrhenius plot: $Ea = 50.4$ kJ/mol.

As shown in Figure 2(b), the catalyst concentration dependence was obtained by making measurements at several catalyst levels ($[Cat] = 1.34 \times 10^{-4}$; 2.67×10^{-5}; and 8.9×10^{-6} mol/L) at a temperature of 80°C. Furthermore, eq. (3) can be simplified by introducing the catalyst concentration into the rate constant:

$$A1 = A[Cat]^b \qquad (4)$$

with $b = 0.6$ and $A = 1.38 \times 10^{10}$ (units to give a rate of mol/L/min).

Figure 2(a–b) shows that a good agreement is observed between predictive molecular weight from the kinetic law (relation 1) and experimental data.

Rheological Kinetics

Combining rheological characterization and kinetic law [eq. (1)] gives the plots of G' and G'' as a function of number molecular weight. Furthermore, at the temperature of 80°C, G' and $G''(M_n)$ are plotted for three catalyst levels [Fig. 3(a)]. Within experimental errors, an identical rheological behavior is observed for these different catalyst levels. This result means that the isothermal viscoelastic behavior of the urethane system throughout the reaction is only dependent of the degree of polymerization. However, the plot of tan δ vs. molecular weight shows a slight quantitative difference between the curves [Fig. 3(b)].

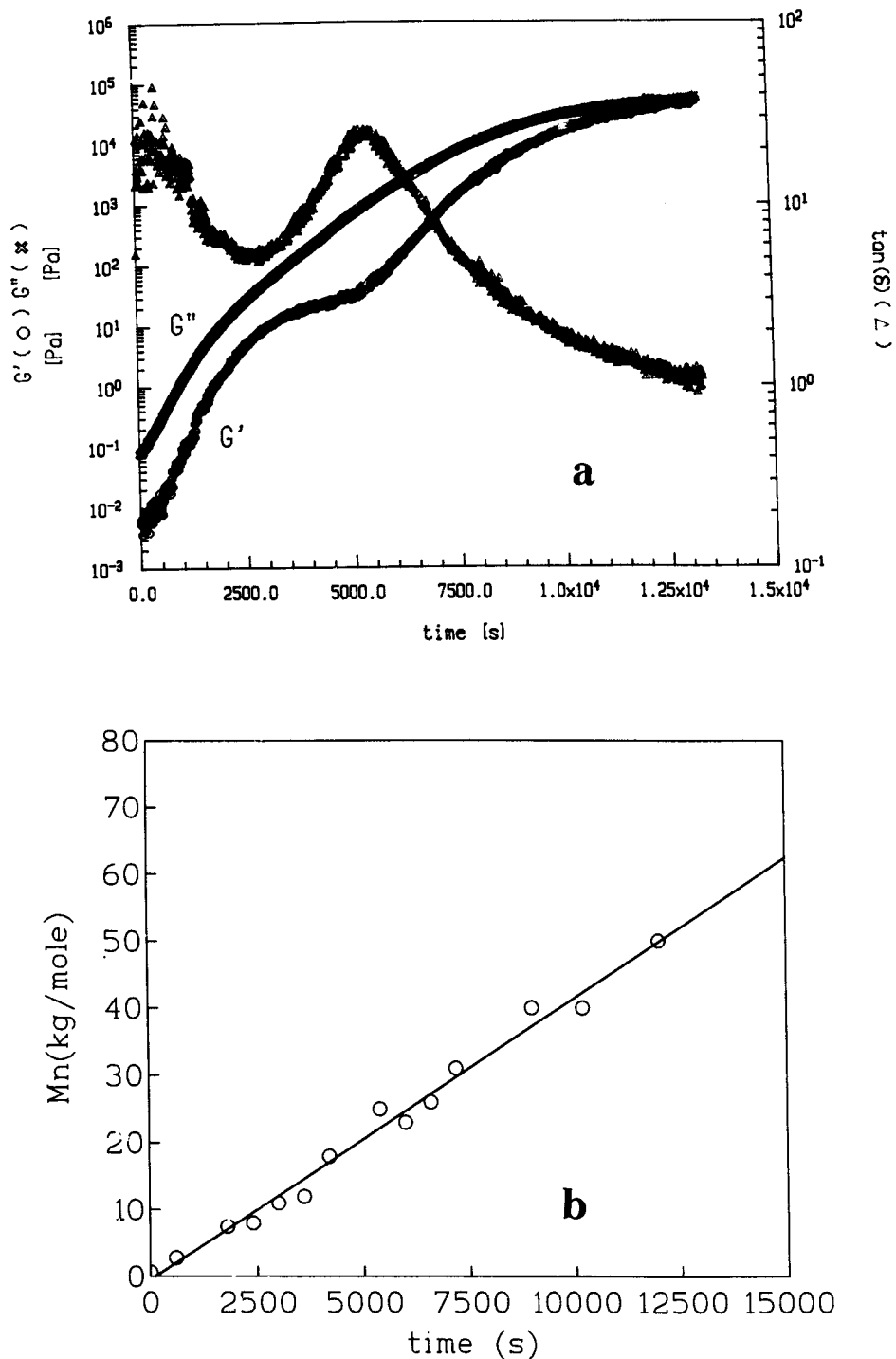On the other hand, as the number molecular weight varies linearly with the reactional time,

Figure 1   Kinetic studies, [cat] = 1.34 × 10⁻⁴ mol/L; ω = 1 rad/s, T = 40°C. (a) Variation of the storage G', loss moduli G'' and $T_g\delta$ vs. time. (b) Variation of the number molecular weight M_n vs. time.

the rheological behavior of the medium throughout the reaction is identical with that described in the general behavior part [Fig. 1(a)]. It is ob-served that with increasing molecular weight, the loss modulus increases while the storage modulus rises sharply until tan δ goes through a minimum
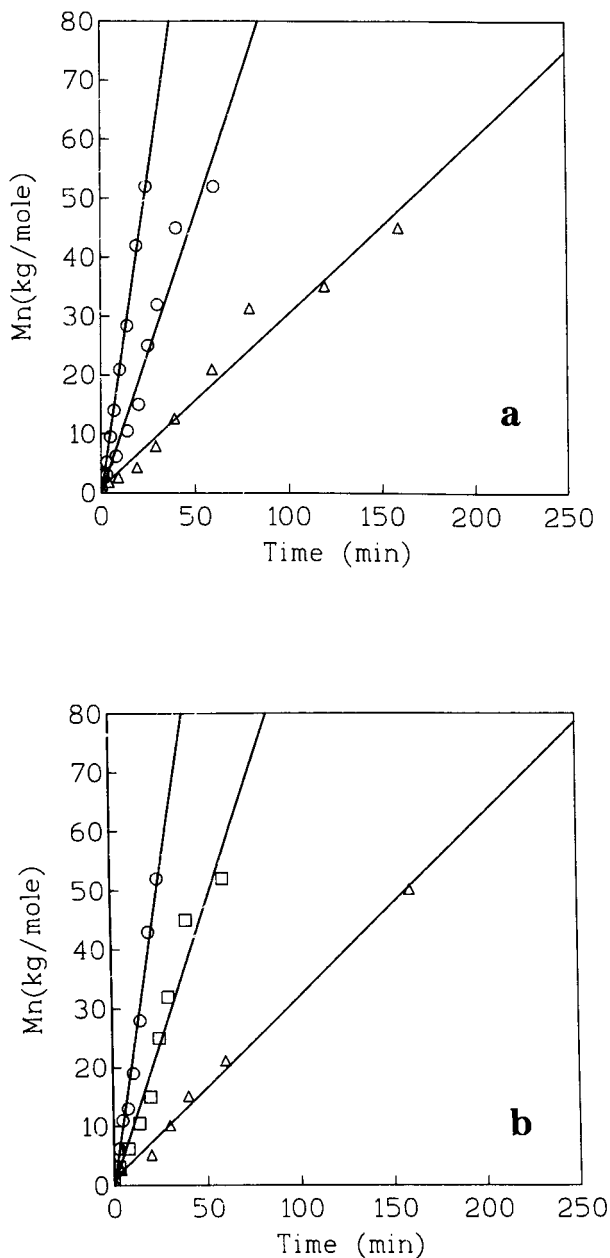
Figure 2 SEC kinetics. Variation of M_n vs. reactional time. (a) Influence of the temperature; [Cat] = 2.67 $\times 10^{-5}$ mol/L. ($\triangle$): 60; ($\square$): 80 and ($\bigcirc$): 100°C. (b) Influence of the catalyst concentration; T = 80°C. ($\bigcirc$): 1.34 $\times 10^{-4}$; ($\square$): 2.67 $\times 10^{-5}$; and ($\triangle$): 8.9 $\times 10^{-6}$ mol/L.

value. The molecular weight at this critical point is readily obtained from tan δ curves and was found to be approximately equal to 102 kg/mol.

At this first stage of the reaction, the urethane system behaves as the rheological changes occurring below the gel point during a crosslinking reaction. However, from the chemical structure of

the two reactants (diol and diisocyanate) and from SEC analysis, possible chemical crosslinks or stars structure of the chains cannot be generated in polyurethane samples. A possible explanation of this rheological behavior is a physical crosslinking of the polyurethane chains through microphase segregation between MDI structure and polyether segments. Indeed, it is well known in the literature that polyurethane blocks copolymers containing alternating flexible and rigid segments generally possess a two-phase morphology due to the thermodynamic incompatibility of the different segment types. In the present study, although urethane system is constituted of soft segments joined end to end by an aromatic structure, rheological behavior prove that a phase segregation can be developed through the association of aromatic groups of the MDI. In addition, the abundance of urethane hydrogen atoms and ether oxygen groups in this polyurethane system permits hydrogen bonding among the polymer chains. The N—H group of the urethane linkage serves as a proton donor while possible proton acceptors are the ether oxygen of the polyether diol.[7,8] As a consequence, hydrogen bonding restricts the mobility of the polyurethane chains segments, and a network structure can develop in the system.

To understand the origin of this physical structure, dynamic viscoelastic experiments were carried out on presynthesized polyurethane samples. Figure 4(a) and (b) show the master curves of the dependence of the storage and loss moduli G' and G'' upon the frequency of the oscillatory shear applied for two presynthesized polyurethane samples of molecular weight M_w = 9.75 and 124 kg/mol, respectively. Viscoelastic behavior [Fig. 4(a)] of the sample having the lowest molecular weight exhibits a low-frequency plateau for the storage modulus. This second plateau can be attributed to a physical network structure formed between the polyurethane chains and confirms the previous assumptions made on hydrogen bonding between the polyurethane chains.

Indeed, this viscoelastic behavior at low frequencies is consistent with the presence of a critical point on tan δ curve as previously observed from rheological changes during urethane polymerization. Nevertheless, Figure 4(b) shows that the viscoelastic behavior of the sample of high molecular weight (M_w = 124 kg/mol) does not exhibit a second plateau. Actually, Figure 5 shows that the presence of this second plateau modulus at
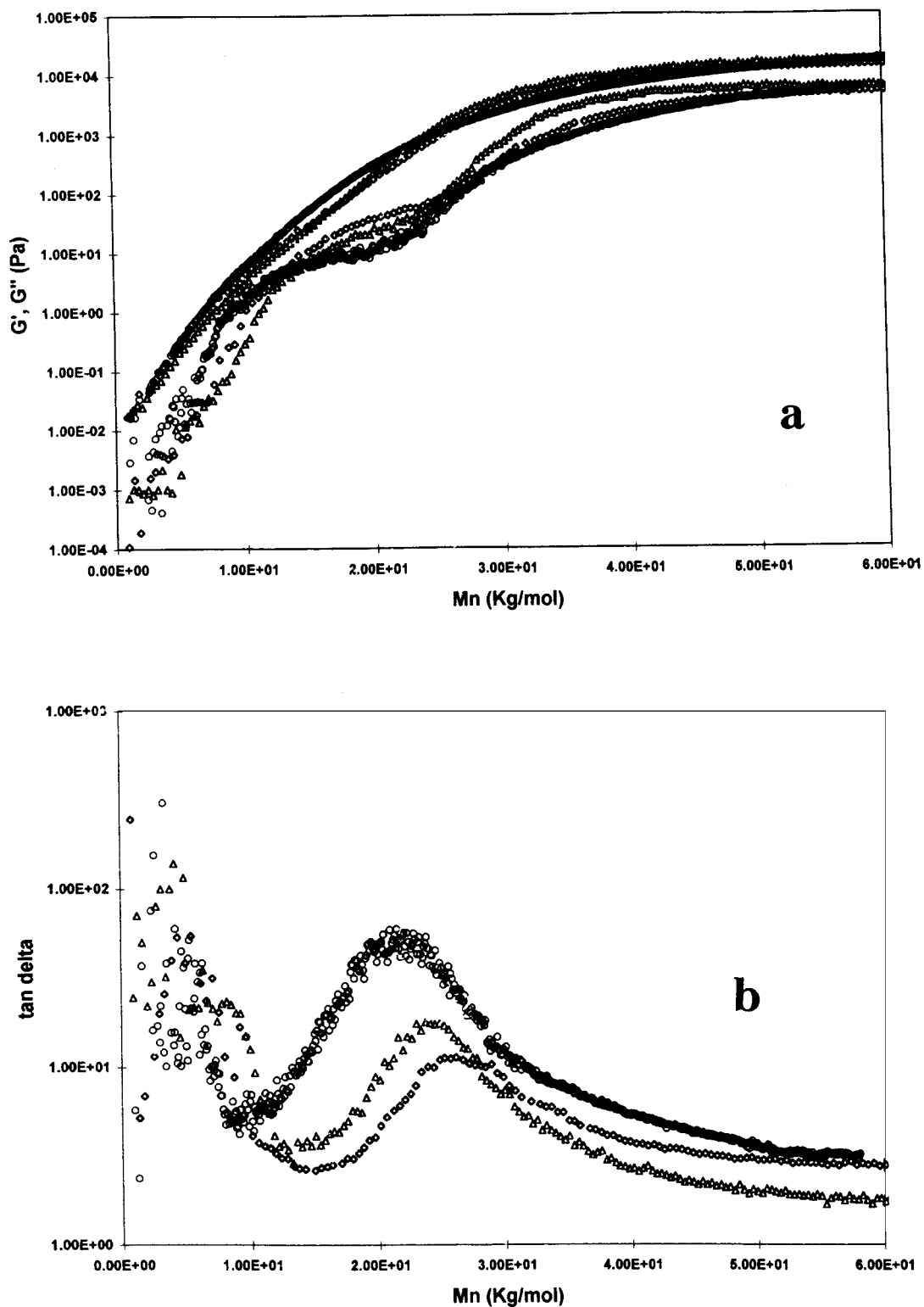
Figure 3 Variation of the rheological parameters vs. number molecular weight at different catalyst concentration; $T = 80°C$; ($\diamond$): 1.34×10^{-4}; ($\triangle$): 2.67×10^{-5}; and ($\square$): 8.9×10^{-6} mol/L. (a) storage G' (M_n) and loss G'' (M_n) moduli. (b) $T_g\delta$ (M_n).
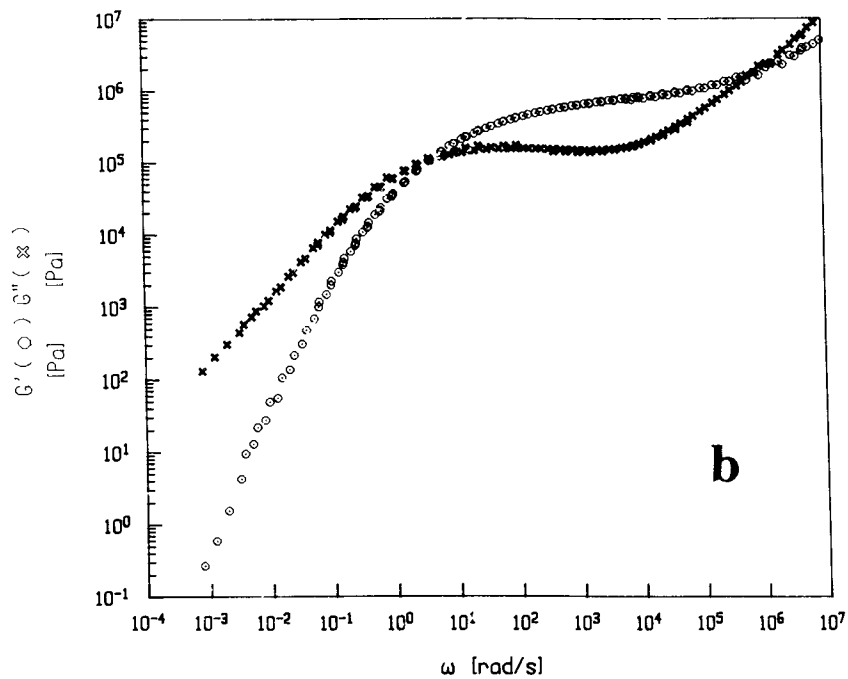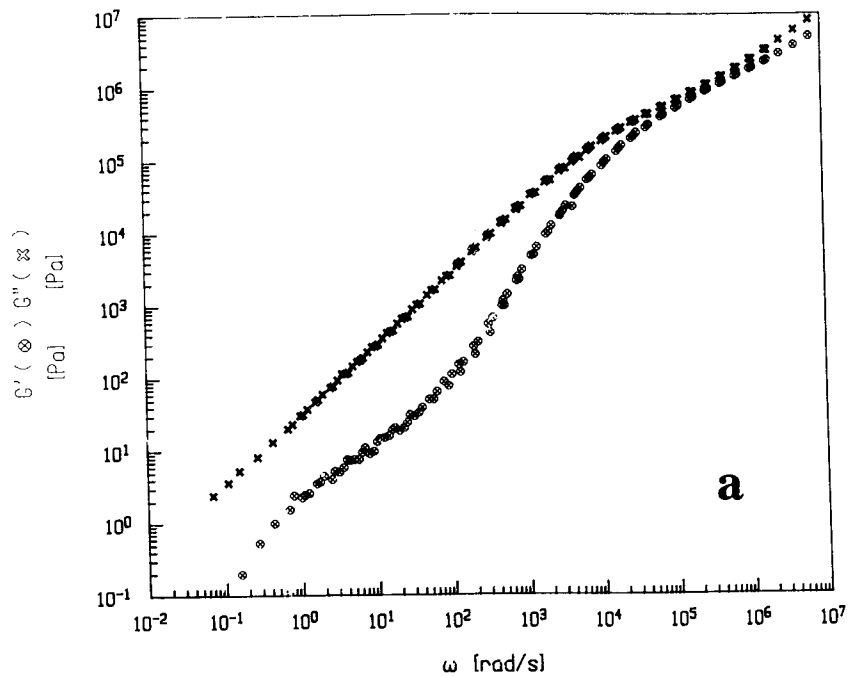
Figure 4   Master curves of $G'(\omega)$ and $G''(\omega)$ at $T = 60°C$. (a) Sample of molecular weight $M_w = 9.75$ kg/mol. (b) Sample of molecular weight $M_w = 124$ kg/mol.
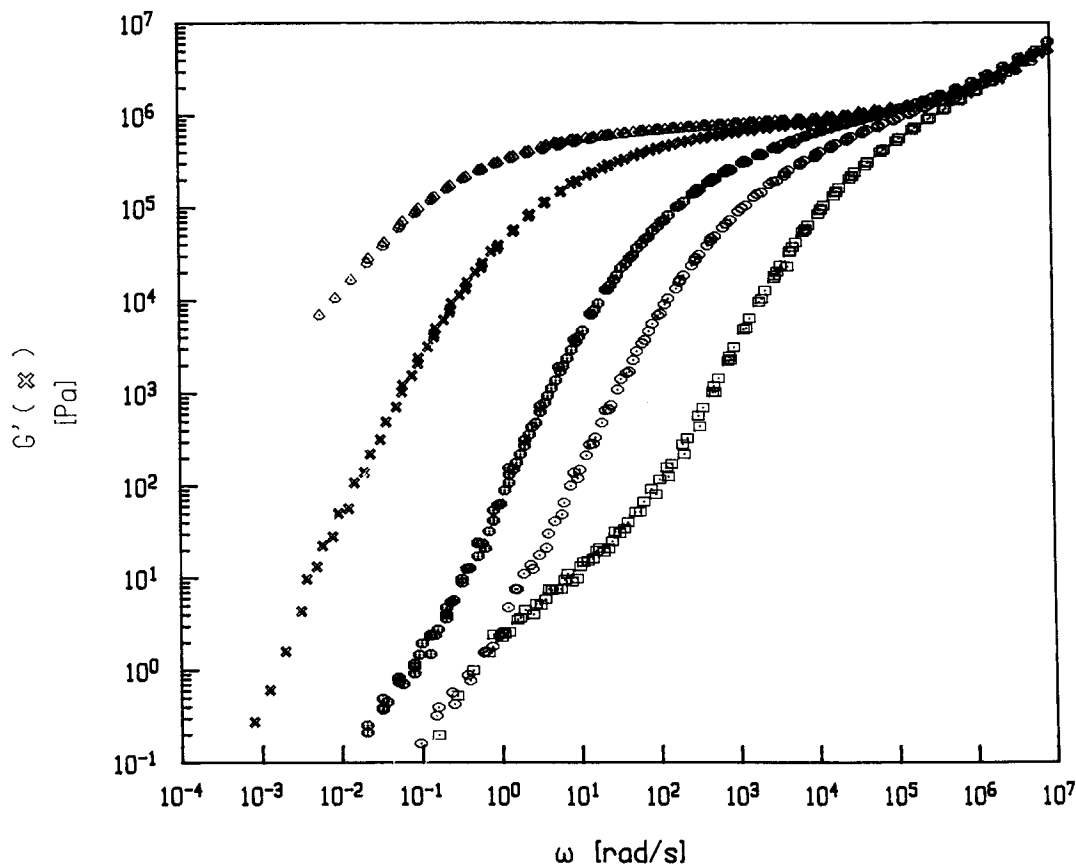
Figure 5   Master curve of $G'(\omega)$ at $T = 60°C$ for samples of molecular weight: M_w = ($\square$) 9.75; ($\odot$) 20; (octagon) 41; (X) 124; and ($\triangle$) 334 kg/mol.

low frequencies progressively vanishes with increasing molecular weight of the prepolymerized samples. Therefore, combining rheological studies on urethane polymerization (Fig. 3) and on prepolymerized polyurethane samples (Figs. 4 and 5) shows that the physical interactions between the polyurethane chains goes through a maximum effect at the molecular weight of 10 kg/mol and vanishes beyond this point with increasing molecular weights.

If the hydrogen interactions are assumed to be effective in the polyurethane system, the fact that the rheological effects of these physical interactions are maximum at molecular weights around 10 kg/mol can be explained as follows: at the initial part of the polymerization process, the reactive system consists of a soup of the different species (oligourethane, unreacted diol, and MDI molecules), as proven by SEC analysis [Fig. 6(a)]. Then, the system consists of oligomeric chains with low hydrogen interactions. As the degree of polymerization increases, the concentration of hy-

drogen bonding increases and the probability of interchain bonding increases, causing a physical temporary physical network. At the onset Me of the topological entangled network, the polyurethane chains are long enough to get entangled in each other. Furthermore, the molecular weight distribution [Fig. 6(b)] shows that a near homogeneous polyurethane system was synthesized. Therefore, the microphase segregation, formed by association of aromatic groups, presents a rheological maximum effect at Mc $\approx$ 2Me. The value of Mc (Mc = 7 kg/mol) is closed to the value of the molecular weight (M = 10 kg/mol), at which the rheological effects are maximum. However, from the value of the secondary plateau modulus (Gs $\approx$ 10 Pa), it can be observed that the contribution to the mechanical properties of this organized structure remains very low compared to polyurethane systems constituted from hard segments, which generally associate to form physical crosslinks (Gs $\approx$ 10^{6-7} Pa).

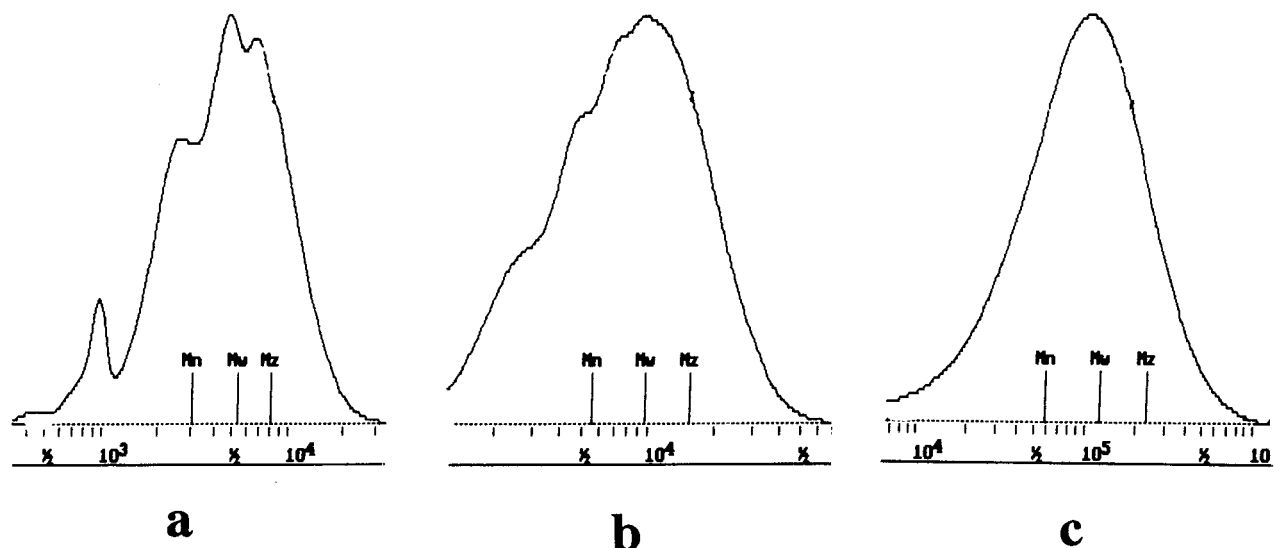With increasing molecular weight beyond Mc,

Figure 6 Molecular weight distribution of polyurethane samples. (a) Initial part of the polymerization process. (b) Onset of entangled chains, $M_w = 10$ kg/mol. (c) Polyurethane of high molecular weight, $M_w = 124$ kg/mol.

the polyurethane chains are strongly entangled due to the attractive Van der Waals forces. Furthermore, the molecular weight distribution analysis [Fig. 6(c)] shows that homogeneous polyurethane was obtained without any tail on the shape of the distribution. On the other hand, it can be observed from Figure 5 that the second plateau vanishes at high molecular weight ($M_w = 124$ kg/mol $\approx 35Me$). This singular behavior is difficulty explainable from these experimental results. However, it can be imagined that the intramolecular hydrogen bonding develops with increasing molecular weight instead of intermolecular hydrogen interactions. Consequently, the physical network due to the intermolecular hydrogen interactions progressively vanishes.

Viscoelastic Properties

The linear viscoelastic properties of polyurethane samples at different molecular weight have been studied. Values of M_w and Ip $= M_w / M_n$ are shown in Table II. In Figure 4(b) are shown the dependence of storage and loss moduli upon the frequency obtained from the well-known time–temperature superposition principle. This empirical procedure was applied from the terminal zone to the end of the rubbery zone just near the glass transition zone ($T_g = -25°C$). As for other linear polymers, the time–temperature superposition principle was found to apply at the present linear polyurethane. Although it was proved in the literature[9] that the apparent

Table II Polyurethane samples, molecular weight (Mw and Ip), Viscoelastic parameters (ηo and J_e^o)

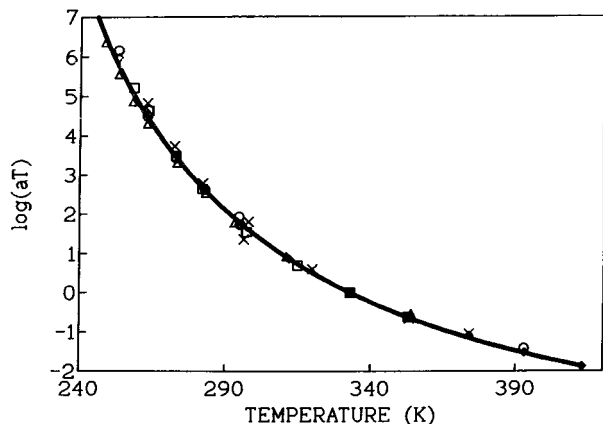| Samples	M_w kg/mol	Ip	ηo Pa·s	ηs Pa·s	J_e^o Pa^{-1}
A	9.75	1.75	3.3×10^1	3.3×10^1	1.0×10^{-2}
B	13	1.83	5.3×10^1	5.0×10^1	5.0×10^{-4}
C	20	2.03	3.3×10^2	—	2.5×10^{-4}
D	28	1.9	1.15×10^3	—	1.2×10^{-4}
E	41	1.95	2.5×10^3	—	1.2×10^{-4}
F	124	2.1	1.35×10^5	—	5.0×10^{-6}
G	146	2.4	3.2×10^5	—	5.0×10^{-5}
H	334	2.7	7.0×10^6	—	3.3×10^{-5}

$T = 60°C.$

Figure 7 Shift factor a_T obtained from five different samples. $M_w =$ ($\triangle$) 9.75; ($\square$) 20; ($\diamond$) 41; ($\bigcirc$) 124; and (X) 334 kg/mol. The reference temperature is 60°C. The solid curve corresponds to the WLF fit.

shift factors obtained did not rigorously obey a single Williams Landel Ferry (WLF) law, a thermorheological simplicity behavior was assumed in this study, which implies the validity of one WLF equation in the range of temperatures $T_g + 5$ and $T_g + 135$°C. This means, as generally assumed in a first approximation in the literature, that the shape of the relaxation process is temperature invariant.

Then, the usual derivation of the WLF equation is:

$$\log(a_T) = -\mathrm{d}\,\frac{2.303c_1^0(T - To)}{c_2^0 + T - To} \qquad (5)$$

where To is the reference temperature ($To = 333$ K in the present study), $c_1^0 = 2.4$ and $c_2^0 = 157$ K. As shown in Figure 7, values of c_1^0 and c_2^0 were obtained by the WLF equation fitting on experimental shift factors a_T of the different samples of Table II. Within experimental uncertainties, the temperature dependence of a_T is the same for all samples.

Calculated values of the plateau modulus G_N^0, obtained by numerical integration over the terminal loss modulus peak:

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega)d \ln \omega \qquad (6)$$

vary slightly around the value of 8.0×10^5 Pa.

As G_N^0 is related to the strand length of the

temporary network consisting of topological entanglements, the plateau modulus lead to an apparent molecular weight between entanglements from the Ferry formula[10]:

$$\mathrm{Me} = \rho RT / G_N^0 \qquad (7)$$

on the order of 3.5 kg/mol.

Me is a constant characteristic of a given polymer melt. For molecular weights greater than Mc $\approx$ 2Me the zero shear viscosity ηo generally increases with the well-known 3.4 power of molecular weight. Indeed, the dependence of isothermal melt viscosity on molecular weight for linear polymers is dominated by the onset of topological entanglement coupling. Then, the values of M_w of Table II show that all the polyurethane samples can be considered as entangled with an entangled density in the range $2.5 \leq M_w/\mathrm{Me} \leq 95$.

Furthermore, for molecular weights greater than M'c $\approx$ 5Me, the recoverable shear compliance, J_e^0, was generally found to be virtually molecular weight independent. However, J_e^0 is known to be very sensitive to the molecular weight distribution and J_e^0 increases with polydispersity.

Values of ηo and J_e^0 can be obtained with the standard linear viscoelastic relation[10]:

$$\eta o = \lim_{\omega \to 0} G''(\omega)/\omega \qquad (8)$$

and

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} G'(\omega)/\omega^2 \qquad (9)$$

In the present study, the assumption region—$G' \sim \omega^2$ and $G'' \sim \omega$—is less well described experimentally, leading to a poorer determination of the limiting parameters, especially J_e^0. Actually, the terminal zone at very low frequencies is significantly affected by the chain interactions due to hydrogen bonding as previously explained. For the lowest molecular weights, it is difficult to reach the terminal region (especially $G' \sim \omega^2$) within a good accuracy and thus to correctly determine the zero shear parameter J_e^0.

The Cole−Cole viscosity plot of Figure 8 shows that two terminal relaxation domains are observed due to the presence of chain interactions. Then, two Newtonian viscosities can be defined as reported in Figure 8. ηo is the Newtonian viscosity observed at the lowest relaxation times and ηos

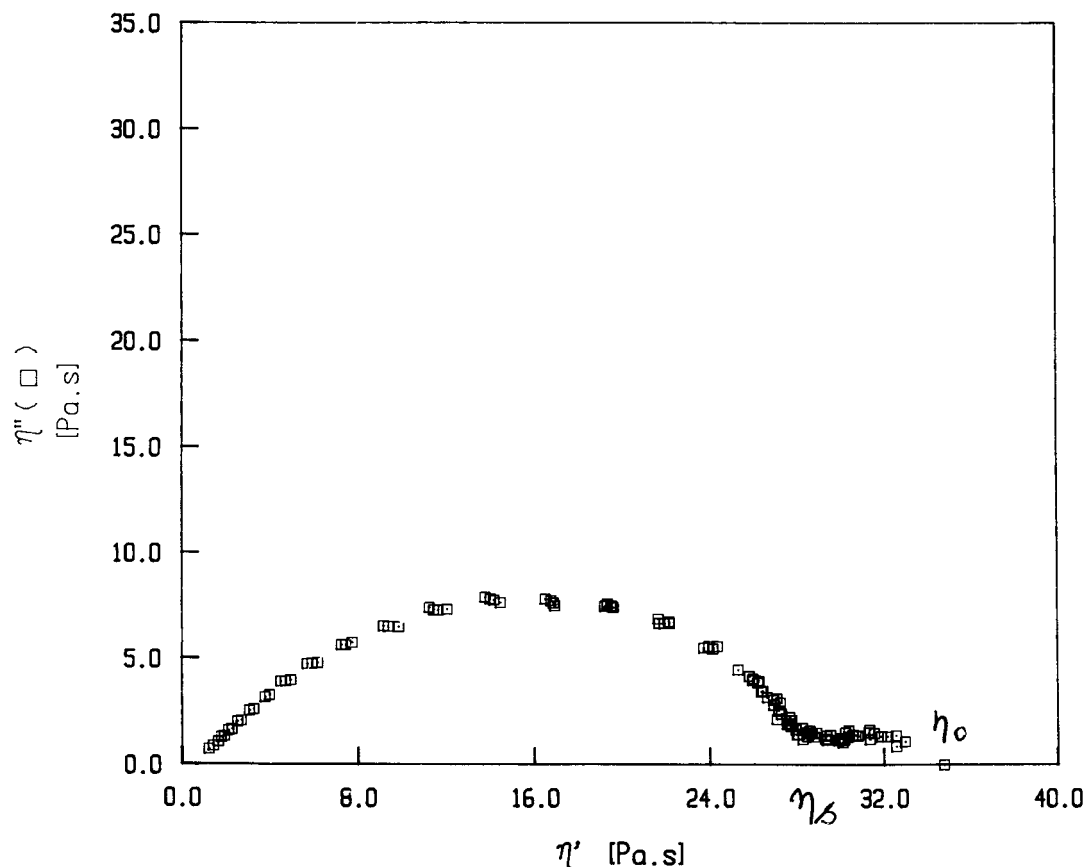**Figure 8** Reduced complex viscosity plot, $\eta''(\eta')$, $T = 60°C$. $M_w = 9.75$ kg/mol.

would be the Newtonian viscosity of the polyurethane fractions without interactions between chains. Values of ηo and ηos are reported in Table II. From these values it can be observed that the zero shear viscosities ηo and ηos are very closed, and the difference vanishes with increasing molecular weights. This result means that the chain interactions slightly perturbed the zero shear viscosity parameter. Furthermore ηo is found to obey the following power law:

$$\eta o = 9.34 \times 10^{-3} M_w^{3.45} \qquad (9)$$

This power law was obtained from linear regression on the logarithmic values of the Table II without values of the samples of low molecular weights ($\eta o \neq \eta os$). Furthermore, the exponent of this power law is slightly higher that the wellkown exponent 3.4 generally observed for linear polymers with a narrow distribution. This difference can be explained by the influence of the broadness of molecular weight distributions as

shown by Montfort et al.[11] on polystyrene samples.

The elastic properties like the steady-state compliance are known to be very sensitive to the molecular weight distribution. Furthermore, as shown in Figure 5, this effect is clearly emphasized at low molecular weights due to the hydrogen interaction between the macromolecular chains. With increasing molecular weights, the compliance J_e^0 decreases and reaches a minimum value (Table I) for the molecular weight $M_w = 124$ kg/mol.This behavior can be attributed to the fact that hydrogen interactions vanishes with increasing molecular weight as previously explained. Beyond this molecular weight, J_e^0 increases with increasing molecular weight. Actually J_e^0 increases with polydispersity. However, from values of J_e^0 it is not possible to rigorously predict a general behavior of the elastic properties because the chain interactions and the polydispersity are correlated from rheological effects point of view.

CONCLUSIONS

Bulk polymerization of urethane made from diphenylmethane-4, 4′ diisocyanate (MDI) and polyether macro diol was investigated in the present work from SEC and rheological studies. It was shown that the kinetics, obtained through SEC experiments, obey a second-rate expression as generally assumed in the literature. In the same way, rheological kinetics were performed using the dynamic shear mode of solicitation. Coupling the rheological characterization and the kinetic law shown that the viscoelastic behavior of the urethane system throughout the reaction is only dependent of the degree of polymerization.

On the other hand, the linear viscoelastic properties of polyurethane samples of different molecular weights were studied. The main characteristic parameters, $\eta 0$, J_e^0 and G_N^0 were determined. Furthermore, the shift factor a_T obtained obey a WLF law.

The rheological study proved that physical crosslinks can be found between the polyurethane chains through association of phenyl structure by hydrogen bonding between urethane group and ether oxygen of the alcohol chains. However, it was shown that these physical interactions increased at the initial part of the reaction. The critical molecular weight, corresponding to a rheological maximum effect of the interactions, was observed closed to the value of Mc = 2Me, characterizing the onset of the topological entanglement coupling. A qualitative explanation of this behavior was attempted. For high entangled polymers, intramolecular hydrogen interactions develop instead of the intermolecular hydrogen bonding.

Then, the structural association of aromatic groups is disrupt and the microphase segregation disappears with increasing molecular weights.

Last, this urethane system will be served as model for academic researches on reactive processing. This kinetic law will allow us to optimize the processing conditions (temperature, catalyst concentration) on this urethane system in an extruder, for example.

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