

Absolute Online Monitoring of a Stepwise Polymerization Reaction: Polyurethane Synthesis

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ABSTRACT: The feasibility of using a recently introduced method for continuous, absolute online monitoring for step-growth polymerization was demonstrated, and polyurethane synthesis was chosen for the demonstration. The previously reported use of this method was for monitoring free-radical initiated chain-growth polymerization. The technique involves continuously withdrawing a small stream of reaction liquid from the polymerization reactor and pumping it through a series of light scattering and viscosity detectors. This permits the absolute weight-average molecular weight and reduced viscosity to be simultaneously monitored as the reaction proceeds. The final weight-average molecular weights of the polyurethane samples were compared to the separate light scattering measurements of the final products. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2070–2077, 2001

Key words: online monitoring of polymerization reactions; time-dependent static light scattering; polyurethane; monitoring; viscosity; light scattering

INTRODUCTION

Static light scattering (SLS) has long been recognized as a preeminent method for absolute determination of the weight-average molecular weight (M_w).^{1–4} Florenzano et al.⁵ recently introduced an online monitoring technique that permits the continuous determination of the absolute M_w and intrinsic viscosity during polymerization reactions. This was accomplished by automatic, continuous extraction of a small sample stream from the reactor and analysis by time-dependent SLS (TDSLS) and single capillary viscometer detectors. No chromatographic columns were needed.

The notion of real-time monitoring is not new; most efforts were concentrated on measuring conversion, radical concentration, or viscosity.^{6–11} Currently, the absolute M_w values are determined after polymerization or at best on aliquots withdrawn during the reaction using size exclusion chromatography^{12,13} (SEC). The online monitoring technique⁵ was applied to chain-growth polymerization of vinyl pyrrolidone⁵ and acrylamide.¹⁴ In this work we applied the online monitoring technique to a step-growth reaction for the first time. A polymerization reaction producing polyurethane was chosen.

The first published work in monitoring a glycol/dibasic acid reaction was made by Flory,¹⁵ who determined molecular weights and rate constants by manually withdrawing aliquots every 10 min during the reaction.

There are several significant differences between the requirements for monitoring step-

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growth and chain-growth polymerization reactions. First of all, in step-growth polymerization the monomer population figures into the computation of the M_w . Hence, it is not necessary to continuously differentiate between the monomer and polymer as is required in chain-growth polymerization. This leads to less stringent requirements on the concentration detection portion of the instrumentation. On the other hand, in step polymerization the M_w is generally lower, especially in the early stages of the reaction. The signal per unit concentration of polymers is thus lower than the case of chain-growth reactions so that sampling and detection procedures must be modified to some degree.

Continuous online monitoring was described in detail in Florenzano et al.⁵ When used for monitoring chain-growth reactions, it is necessary to know both the total concentration of solute arriving at the detectors and the fraction that is composed of monomer. This was accomplished by using a refractometer (RI) to measure the total solute concentration (which varies because of extraction pump inefficiency as the reaction solution becomes more viscous during polymerization) and an UV detector for following the disappearance of the monomer double bonds as monomer is incorporated into the polymer chains. In such reactions the differential refractive index increment (dn/dc) of both the monomer and polymer must be known. A technique for simultaneously determining the monomer and polymer dn/dc was recently introduced.¹⁶ The major difference in urethane polymerization was that the reactor contents were pumped at full concentration through the detector train, which consisted of an absolute LS intensity monitor for TDSLS and a single capillary viscometer. For a step-growth reaction it was no longer necessary to distinguish between monomer and polymer concentrations in computing the M_w ; and, because no dilution of the reactor liquid was used, there was no need to monitor the total solute concentration, because it remained constant.

Thus, the TDSLS signal alone allowed the computation of the absolute M_w after correction for the second virial coefficient (A_2). The A_2 correction was found by separate LS measurements on polyurethane.

The degree of polymerization (DP) and the molecular weight of the step polymerization cannot exceed a certain value, depending on the stoichiometry of the initial solution. The reaction cannot proceed any further when all the chains ending

with the less abundant monomer link up so that all chains have the more abundant monomer at their ends. The theoretical limits on the number-averaged (DP_n) and weight-averaged (DP_w) degrees of polymerization are¹⁷⁻¹⁹

$$DP_n = (1 + r)/(1 - r) \quad (1)$$

$$DP_w = (1 + r)/(1 - r) + 4r/(1 - r^2) \quad (2)$$

where r is the initial ratio of the concentration of the less abundant monomer to the more abundant one, and B is defined as the more abundant species, so that

$$r = [A]_0/[B]_0 \quad (3)$$

Thus, r is always less than or equal to 1. The corresponding molecular weights (MW) are

$$M_n = [(DP_n - 1)MW_a + (DP_n + 1)MW_b]/2 \quad (4)$$

$$M_w = [(DP_w - 1)MW_a + (DP_w + 1)MW_b]/2 \quad (5)$$

Here MW_a is the molecular weight of the stoichiometrically less abundant monomer and MW_b is the molecular weight of the more abundant comonomer. In this work the stoichiometrically less abundant monomer was tolylene diisocyanate (TDI, $MW_a = 174.16$), and the more abundant one was ethylene glycol (EG, $MW_b = 62.07$).

EXPERIMENTAL

Materials

The monomers EG (OHCH₂CH₂OH), and TDI (NCOC₆H₃CH₃NCO) and the solvents dimethyl sulfoxide (CH₃CH₃SO, DMSO) and dimethyl formamide (CH₃CH₃NCHO, DMF) were Aldrich products and were used without further purification. The reaction compositions are given in Table I.

Because some EG was withdrawn from the system before the addition of the TDI, the exact stoichiometry depended not only on the amounts of the two monomers introduced but also on the duration and rate of EG withdrawal prior to the addition of the TDI. This was taken into account in the computations.

Table I Polyurethane Reactions

| File Name | EG (g) | DMSO in EG (g) | TDI (g) | DMSO in TDI (g) |
|-----------|--------|----------------|---------|-----------------|
| h0419a01 | 7.8042 | 50.0085 | 14.7465 | 40.3548 |
| h042000 | 3.9182 | 25.1913 | 8.8343 | 21.9134 |
| h0421a01 | 3.9295 | 45.1570 | 8.6782 | 21.7282 |
| h0503a01 | 3.9352 | 45.3659 | 9.1707 | 21.5779 |
| h0504a01 | 3.4929 | 35.5681 | 7.9794 | 20.8951 |
| h0505a01 | 3.5140 | 26.6298 | 7.7949 | 19.2504 |

Polymerization

Fine DMF was chosen as a solvent at the beginning of the synthesis. The dn/dc value of the polyurethane in DMF solution was only 0.003, which produced an optical contrast between the polymer and solvent that was detected within the error bars of the TDSLIS instrument. The dn/dc of polyurethane in DMSO was 0.1017, which produced acceptable optical contrast. Monitoring work was therefore continued in DMSO.

The reaction vessel was a 200-mL flask initially containing EG solution in DMSO. The pump initially drew from a separate vessel containing pure DMSO at room temperature in order to stabilize the detectors and obtain a baseline. After stabilization

the pump was switched to withdrawal from the reaction vessel, which was likewise at room temperature (except for reaction h0419a01). The comonomer TDI solution in DMSO (also at room temperature) was added while vigorously mixing the EG solution. The reaction started immediately and the temperature rose to 65°C, because of the exothermicity of the reaction. Gradually, the temperature of the reaction vessel was increased to 120°C via circulation of heated silicon oil and kept at this temperature for 1.5–2 h. The reaction mixture was pumped undiluted into the detector train at a typical flow rate of 0.5 mL/min. In traversing the pump and tubing leading to the detectors the sample stream was effectively cooled to room temperature by the time detection of the continuously flowing reactor solution was made. Hence, variations in physical constants, such as dn/dc and A_2 , were presumed to be negligible in the detection phase, despite wide changes in temperature in the reactor during the reactions.

In reaction h0419a01 (Table I) the EG solution was heated to 115°C and the TDI solution was added when the system was hot. However, in all other experiments the EG solution was kept at room temperature and TDI was added at room temperature.

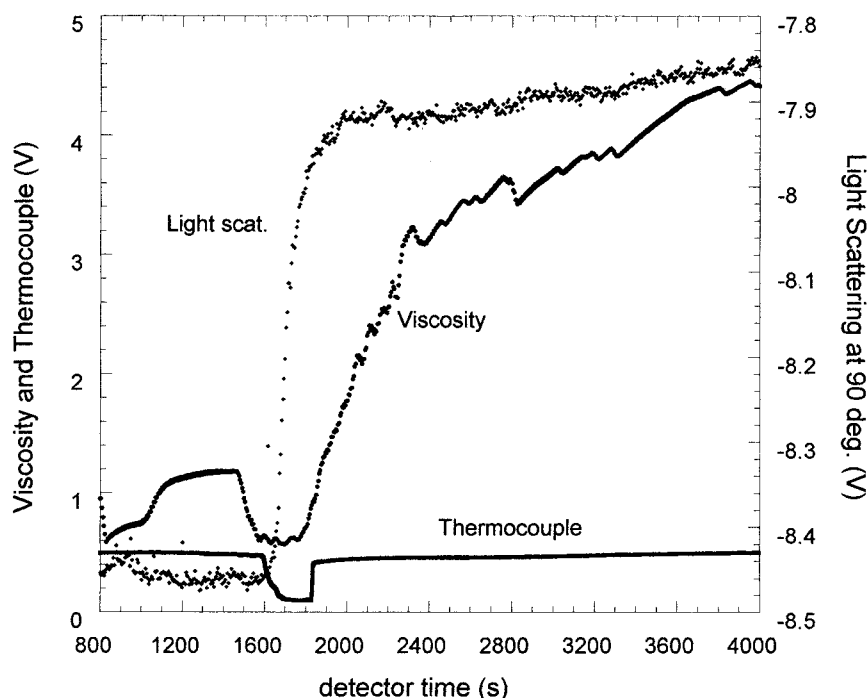


Figure 1 The raw viscosity, temperature, and light scattering data (90°) of the h0419a01 experiment.

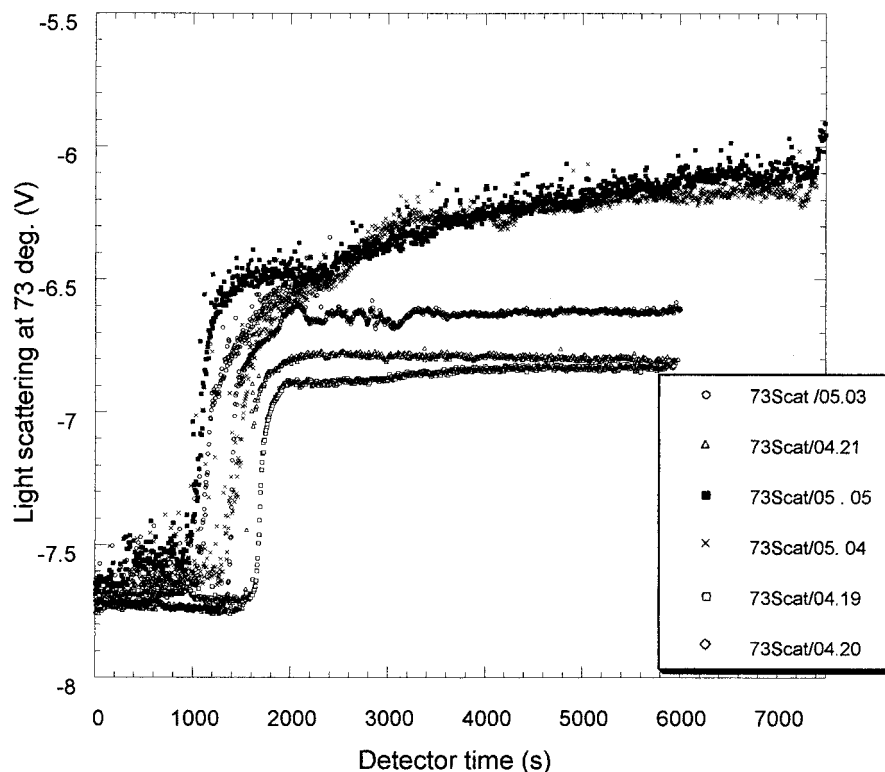


Figure 2 Raw light scattering data during the different polyurethane synthesis reactions shown in Table II.

At the end of the reaction period the pump was stopped and 5–10 mL of ethanol was added to the reaction vessel to stop the reaction. The polyurethane end product was then precipitated by pouring it into water, after which it was filtered and dried in a vacuum oven.

Detector System

The home-built TDSLS and viscosity detectors were previously described in detail.^{5,20,21} The TDSLS detector was constructed from black, round, Delrin plastic stock. The absolute scattering was simultaneously monitored from seven angles from 35° to 141° via optical fibers mounted flush to the interior of the cylindrical scattering chamber. The diameter of the scattering chamber was 5 mm, and the total sample volume about 90 μL . A 25-mW vertically polarized diode laser (Laser Max, Inc., Rochester, NY) operating at 677 nm provided the incident light to the chamber. High sensitivity, low noise photodiodes detected the scattered light collected by the optical fibers. The photodetectors were provided by Brookhaven Instruments Corporation (Holtsville, NY).

In fact, because the amount of polyurethane produced in these reactions was so small (<10 kg/mol), it would be sufficient to use a single angle LS detector to monitor the M_w during the reaction.

The temperature of the reaction vessel was monitored with a K-type probe.

The sample removed from the reaction vessel was pumped into the detectors without dilution. The low molecular weights in these experiments required the use of higher concentrations for the LS measurements. In step-growth polymerization the polymer concentration is the sum of the concentrations of the two monomers. Its value in the reactor vessel was constant after the addition of the second monomer. Because the reaction fluid was pumped to the detectors without dilution, the polymer concentration in the detector had the same value.

The M_w was computed by the usual Zimm^{1,2} single contact approximation,

$$Kc/I(c) = 1/M_w + 2A_2c \quad (6)$$

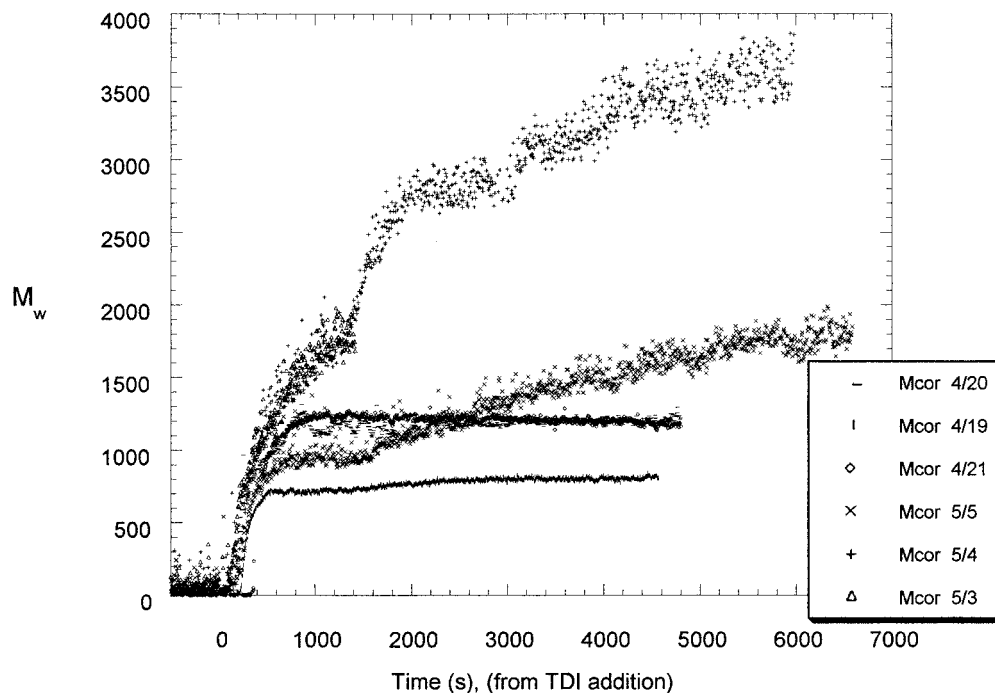


Figure 3 The online measured M_w during polyurethane synthesis.

where $I(c)$ is the excess Rayleigh scattering ratio, c is the polymer concentration, and K is an optical constant given for vertically polarized light by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \quad (7)$$

where n is the solvent index of refraction and N_A is Avogadro's number. The dn/dc for polyurethane in DMSO is 0.1017. The usual angular dependent term $q^2 \langle S^2 \rangle$ in eq. (6) is omitted because the polyurethane molecules have such small

mean square radii of gyration $\langle S^2 \rangle$ that they can be considered to scatter isotropically in the scattering plane.

The A_2 was determined independently in separate static LS measurements of the final product. It was found to be $0.00223 \text{ cm}^3 \text{ mol/g}^2$. Hence, determination of the $I(c)$ at every point in time allows the M_w to be obtained as a function of time during the experiment according to eq. (6).

The viscometer was a single capillary mounted via T connectors to a Validyne Engineering differential pressure transducer. The voltage output of

Table II Diol/Diisocyanate Ratios, Maximum Allowed Molecular Weights, Online Measured Molecular Weights, and Separately Measured Values

| File Name | Molar Ratio | Critical Monomer | Maximum Allowed | | | | Online Measured M_w | Final M_w by LS |
|-----------|-------------|------------------|-----------------|--------|-------|--------|-----------------------|-------------------|
| | | | DP_n | DP_w | M_n | M_w | | |
| h0419a01 | 0.744 | TDI | 6.8 | 13.5 | 748 | 1,350 | 800 | — |
| h042000 | 0.976 | EG | 76 | 152 | 8,970 | 18,000 | 1,300 | — |
| h0421a01 | 0.901 | TDI | 19 | 38 | 2,210 | 4,470 | 1,400 | — |
| h0503a01 | 0.946 | TDI | 36 | 72 | 4,210 | 8,470 | 1,900 | 1,922 |
| h0504a01 | 0.953 | EG | 42 | 84 | 4,900 | 9,850 | 3,500 | — |
| h0505a01 | 0.961 | TDI | 50 | 100 | 5,840 | 11,730 | 2,800 | 2,741 |

The molar ratio is of the critical monomer to the more abundant one after taking into account the EG lost via withdrawal from the reactor before TDI is added.

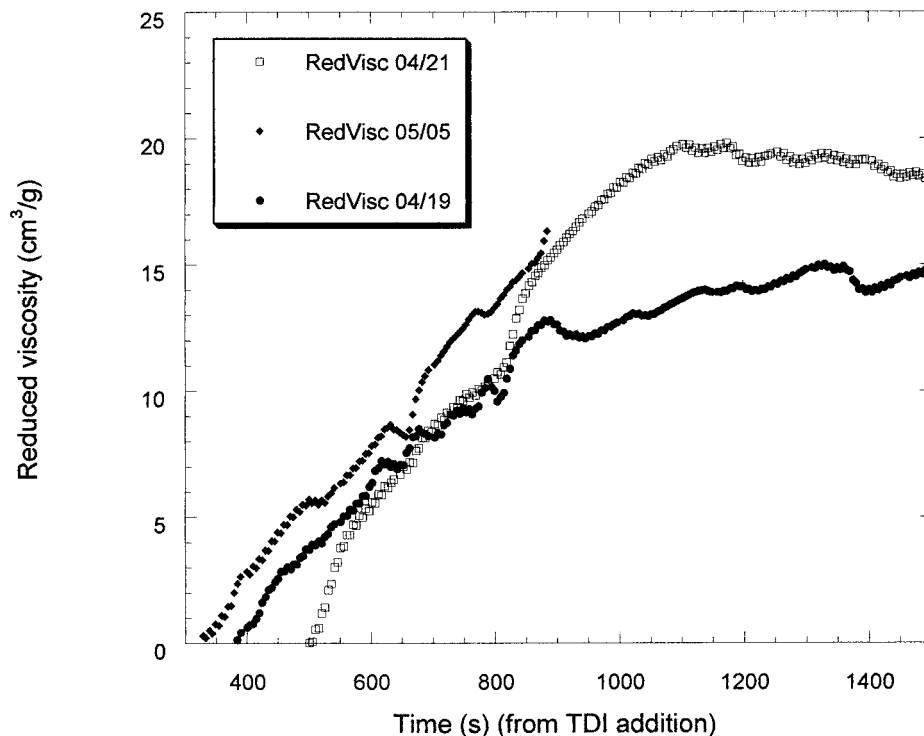


Figure 4 Reduced viscosity versus the time for several of the polyurethane synthesis reactions.

the transducer was directly proportional to the pressure drop across the capillary, which was proportional to the solution viscosity. This system allowed the direct computation of the reduced viscosity (η_r) at each point in time t by

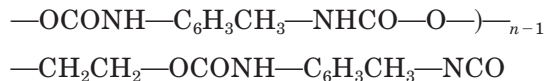
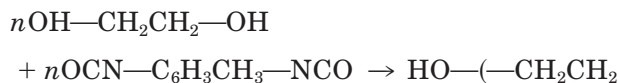
$$\eta_r(t) = \frac{V(t) - V_b}{cV_b} \quad (8)$$

where V_b is the viscometer baseline voltage, $V(t)$ is the voltage at time t , and c is the concentration, which is constant throughout the polymerization.

The delay time between the withdrawal of solution from the reactor and measurement by the detectors was about 170 s.

RESULTS

The polyurethane synthesis proceeded with formation of carbamate (urethane) bonds by the reaction of isocyanates and alcohols as follows:



The raw viscosity, temperature, and LS data of experiment h0419a01 (Table I) are given in Figure 1. At the outset only pure DMSO was pumped. At 829 s (reactor time) the system was switched to the glycol solution, which was observed as an increase in the viscosity signal. The temperature of the system was initially 115°C (thermocouple reading at 0.47). Diisocyanate solution was added at 1430 s, which was followed by a sharp decrease in the viscosity and temperature signals. As the diisocyanate reacted the viscosity, temperature, and LS all increased. The LS signal started to sharply increase at 1600 s, which was followed shortly afterward by the viscosity signal increase.

The raw LS data for the six reactions studied (Table I) are given in Figure 2. The corresponding values of the M_w are given in Figure 3. The final molecular weights obtained from separate LS measurements and online measurement and the stoichiometrically allowed maximum M_w are given in Table II. The precipitated endproducts of

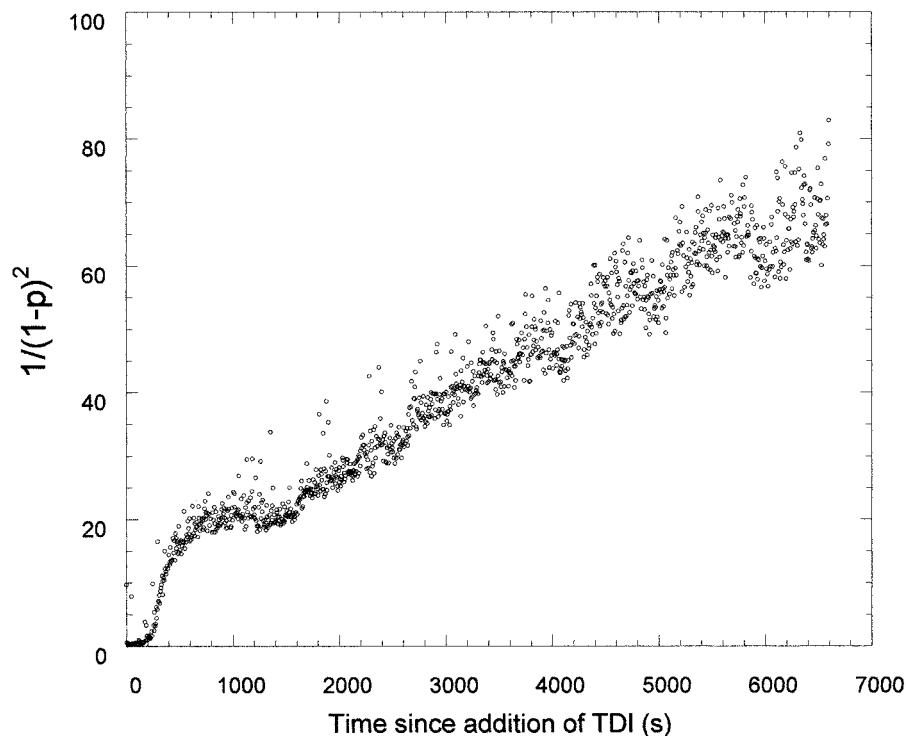


Figure 5 Reaction kinetics of h0505a01 (Table I).

two of the reactions were subsequently analyzed by batch light scattering. The agreement between the batch determination and the final online values was good.

Figure 4 shows the reduced viscosity versus time for several reactions. The abrupt cutoff for 05/05 corresponds to viscometer saturation.

These experiments showed that, as expected from a step-growth reaction, the molecular weight increased with time. This stands in contrast to chain-growth reactions where, in the ideal case, the M_w starts at a maximum value and decreases as the reaction proceeds. At a given temperature the reactions tended to slow down before theoretical maximum molecular weights were obtained. An increase of the reactor temperature resulted in increased molecular weight. However, none of the reactions reached the maximum value of M_w permitted by the value of r .

Because the temperature varied widely during the experiments, which was due to the various processes of adding reagents and temperature increases from reaction exothermicity and external heat input from the circulating bath, we did not expect the kinetics to follow well-defined models. Furthermore, the increasing viscosity of the solutions with an increasing degree of polymerization

led to a decrease in the reaction rate, which was also not accounted for in simple kinetic schemes. Nonetheless, it is still worth considering such schemes in examining the data.

The kinetics of step polymerization reactions can be derived from the molecular weights. The extent of the reaction p , defined as the ratio of the unreacted groups of the less abundant monomer to the total number of such groups, and the DP_n are related by

$$DP_n = \frac{1+r}{1+r-2rp} \quad (9)$$

where r is the stoichiometric ratio of the less abundant monomer to the more abundant comonomer. High polymer is possible only when r is close to one. Under these conditions the molecular weight and degree of polymerization are related as

$$DP_w = (1+p)DP_n \quad (10)$$

The p is defined as the ratio of the concentration of the unreacted bonds of the stoichiometrically

less abundant monomer to its initial value, which is approximately

$$p = \frac{(\text{DP}_w - 1)(1 + r)}{2r\text{DP}_w + 1 + r} \quad (11)$$

Because, as noted, the temperature of the first phase of the reactions was not at constant temperature, they could not be fitted to any meaningful kinetics.

The reaction rate depends on the fraction of unreacted end groups $(1 - p)$. When an external catalyst was used, the reaction rate was proportional to $(1 - p)^2$; but when the reaction was self-catalyzed, it was proportional to $(1 - p)^3$. Integrating the rate equation one obtains¹¹

$$\frac{1}{(1 - p)^2} = 2[M]_0^2 kt + 1 \quad (12)$$

Figure 5 shows the plot of $(1 - p)^{-2}$ versus time for the reaction h0505a01. The plot gives a straight line after the temperature was stabilized at 115°C at 1500 s until 6500 s, when the temperature was further increased. This straight line indicates that the reaction followed the third-order self-catalyzed kinetics.

CONCLUSION

The online monitoring of urethane polymerization was achieved by following the LS intensity at a single angle of a LS detector through which a small reaction stream continuously flowed. Addition of an inexpensive single capillary viscometer provided complementary information. Although the reactor temperature varied widely because of the addition of reagents, the reaction exothermicity, and externally applied heat, the detectors themselves and the reactor liquid reaching them were essentially at room temperature, so that the constants needed to compute the M_w at the detectors (dn/dc and A_2) did not vary substantially. Thus, the technique provides a robust means of monitoring step-growth reactions, even when

there are considerable thermal fluctuations in the reactor.

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