Onset of Phase Separation in Segmented Urethane Polymerization

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Synopsis

The development of heterogeneous structure during the polymerization of a polyurethane system using a polyether diol of $\overline{M}_n$ = 2000 as the soft segment and 4,4'-diphenylmethane diisocyanate extended with 1,4-butanediol as the hard segment was monitored following the amount of light transmitted by the sample and the increase in viscosity of the reacting mixture. The amount of light transmitted by the reacting sample was observed to decrease sharply at a given point in the reaction. The cloud point was taken as the onset of phase separation in the system and the number average sequence at this point was found to be fairly constant at about 1.3 independent of reaction temperature and system composition. In many cases, the cloud point occurred at quite low conversion, meaning that a significant amount of subsequent polymerization occurs in a heterogeneous medium. It was also found that the viscosity of the material reached very large values at partial conversions of the monomers and presented throughout the reaction values larger than those expected from an increase in molecular weight alone. Viscosity is apparently sensitive to a different aspect of the phase separation process than the light transmission.

INTRODUCTION

The thermoplastic urethanes are block copolymers of the type $(AB)_n$.[1] The hard segments are composed of short polyurethane sequences of relatively low mobility which are interconnected by flexible polyester or polyether based soft segments. The two different segments form independent phases and are responsible for the general mechanical characteristics of these systems.

Considerable effort toward the understanding of phase separation and structure properly relations has been made in the past few years[1,2] and several models of phase segregated polyurethane systems have been proposed.[3-7]

With development of reaction injection molding (RIM) as a new process for polyurethanes, a fundamental understanding of the polymerization process and its relationship to the development of phase segregated structure has become important.[7,8] A complete description of the RIM process is given elsewhere.[7,10] Suffice it to say here that RIM, is based upon the impingement mixing of a diisocyanate and a mixture of polyfunctional hydroxyl compounds. The liquid monomer mixture flows into the mold at fairly low pressure and rapidly reacts to form a solid article of the desired shape *in situ*. The heat transfer characteristics make for highly non-uniform reaction conditions in the mold.[7] This in turn affects the molecular structure and morphology of the polyurethane material formed from point-to-point within the mold.

In this study, the isothermal polymerization of a polyether diol/diphenyl-

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methane diisocyanate/butanediol was followed by two different techniques, monitoring of light transmission and viscosity, in order to obtain some fundamental information about the *onset* of phase separation during the reaction and how the onset depends on the polymerization conditions. The main two experimental variable were the urethane composition and temperature of the system.

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EXPERIMENTAL

Chemical System

The polyurethane system used in this study consisted of a polyether soft segment (PPO-PEO 1256 Niax Polyol, Union Carbide Corporation) with 30.4 wt % polyoxyethylene as an end block on polyoxypropylene, with a functionality of 1.96 and $\overline{M}_n$ = 2000, and a hard segment based either on pure 4,4′-diphenylmethane diisocyanate (MDI, Mondur M, Mobay Chemical Company) or a mixture of 4,4′-diphenylmethane diisocyanate and trifunctional cycloaducts (Isonate 143L, The Upjohn Company) and chain extended with 1,4-butanediol (BDO, Union Carbide Corporation). The 143L system has a functionality of ca 2.2 (ref. 11) and is liquid at ambient temperature.[12] It was used in this study because it is commonly used in commercial systems and is easier to handle than the pure MDI.

The polyol and the BDO were degassed at 60°C for several hours before being used. The MDI was purified by heating it to 60°C and filtered before use. The liquid form (143L) was used as received. A similar system and procedures have been used by Zdrahala et al.[13] in other studies concerning polyurethane elastomers.

Light Transmission

Figure 1 shows a schematic representation of the experimental setup. A copper cell holder with water or ethylene glycol circulation was used to control the temperature during the reaction. Two circular glass plates with a diameter of 25 mm and a thickness of 5 mm were used as a reaction cell with a 1-mm Teflon spacer. The upper plate had two drilled holes for injection of the sample. The turbidity of the sample was monitored with a photocell (CL-702, Clairex Co.), using a 30 W white light source. The intensity of the light transmitted by the
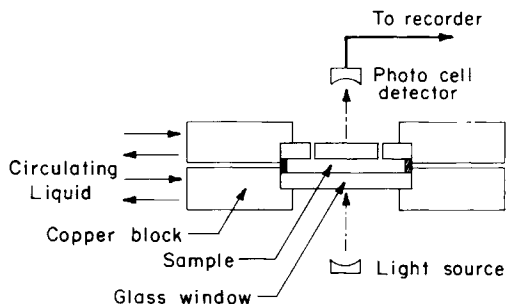

Fig. 1. Schematic representation of the light transmission apparatus.

sample was recorded as a function of time. The achievement of isothermal conditions was confirmed by inserting a thermocouple between the plates.

Three different stoichiometric ratios and five different temperatures were investigated: the mole ratios of MDI/BDO/PPO-PEO were 5/4/1, 5/3/2, and 5/2/3 and the reaction temperatures were 25C (143L), 55C (143L and pure MDI), 80C (pure MDI), 95C (143L), and 110C (143L).

The two diols were weighed in an analytical balance in the desired proportions and kept in a constant temperature bath at the reaction temperature ($\pm 3°C$). The diisocyanate was always measured by volume (the mole ratio of the two diols was a more crucial variable in these experiments than the overall OH/NCO stoichiometry, the latter affecting primarily the final molecular weight development in the last stages of the reaction). The reactive species were mixed with a mechanical stirrer for 30 sec and then injected with a syringe into the cell. Time zero of the reaction was taken as the moment of addition of the diisocyanate. All the reactants were very thoroughly mixed together before they were injected. The maximum elapsed time between addition and injection into the cell was one minute. To provide enough time to observe the dynamics of phase separation during the polymerization, no catalyst was used in these experiments. The intensity of light transmitted by the sample was recorded for at least 1 h.

Viscosity Rise

Isothermal viscosity measurements were done on a Rheometrics Mechanical Spectrometer (RMS) using a 50-mm-diam plate and cone-plate angle of 0.04 rad. The materials were run without catalyst to allow time for injecting them into the RMS.

One stoichiometric molar ratio of MDI (143L)/BDO/PPO-PEO, 5/4/1, was investigated at several temperatures. As in the previous case the polyol and BDO were weighted and the diisocyanate added by volume. The components were mixed for 30 s and then a 1.5 cm^3 sample was transferred with a hypodermic syringe into the cone and plate. The viscosity rise was obtained as a function of time. Small sample sizes and long reaction times, insured that nonisothermal effects due to the heat of reaction would be negligible. The liquid form of MDI (143L) was used in all of these rheological experiments.

RESULTS AND DISCUSSION

Light Transmission

A typical curve for this experiment is shown in Figure 2. In general, it was observed that shorter "times for opacity" t_o and higher rates of intensity loss corresponded to higher temperatures and/or higher hard segment concentration. The time to opacity parameter was determined as indicated in Figure 2 from the intersection of the "preturbidity" horizontal line with the steepest slope in the dropping transmittance region. We note that the increase in turbidity begins very abruptly, indicating that it very likely corresponds to a critical point for the development of optical inhomogeneities.

In order to quantify these results it was assumed as a first approximation that the polymerization proceeded homogeneously up to the point at which the in-
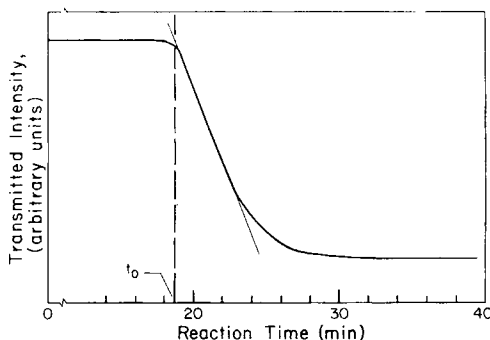
Fig. 2. Typical plot of transmitted light vs. reaction time (for MDI/BDO/PPO-PEO = 5/3/2 at 55°C).

tensity of the transmitted light began to drop.   The time for opacity, or cloud point, then corresponds to segragation of structures of size sufficient to scatter light.   Since before segregation the reaction was considered homogeneous, the average sequence length of the sample was calculated from the homogeneous polymerization model, using the recursive approach of López-Serrano et al.[14] In this case the most important variable to quantify was the number average sequence length of hard segments given in terms of composition variables by

$$N_n = 1/(1 - r_1 q_1^2) \tag{1}$$

where r_1 is the ratio of moles of BDO to MDI at zero conversion and q_1 is the fractional conversion of BDO hydroxyl groups.

The dependence of time in this equation was introduced using the following kinetic scheme for overall group reaction:

$$A + B \xrightarrow{k_1} A-B$$
$$\tag{2}$$
$$A + C \xrightarrow{k_2} A-C$$

where A is an isocyanate group, B is a hydroxyl group belonging to the BDO, and C is a hydroxyl group from the polyol.   It is implicitly assumed here that the reactivity of a given group is not affected by the nature of the parent molecule.

López-Serrano et al.[14] present a detailed analysis and derive general differential equations governing the kinetics of this system.   Macosko and co-work-

TABLE I
Summary of Light Transmission Results for Systems Using Pure MDI

Temperature (°C)	Molar ratio MDI/BDO/PPO	Segregation time (min)	Fractional conversion	Number average seq. length	
55	5/4/1	6.3	0.43	1.17	
	5/3/2	18.5	0.59	1.26	
	5/2/3	39.0	0.70	1.24	$\bar{x} = 1.22$
80	5/4/1	2.5	0.43	1.17	
	5/3/2	8.3	0.64	1.32	
	5/2/3	16.3	0.71	1.25	$\bar{x} = 1.25$

ers[15-17] have estimated the kinetic constants shown in eq. (2) by adiabatic temperature rise and infrared spectroscopy and have shown that it is adequate in most cases to assume $k_1 = k_2 = k$. The value of k for this system is given by Castro and Macosko[16] in Arrhenius form

$$k = k_0 \exp(-E/RT)$$

with $k_0 = 6.64 \times 10^5$ (g/mol OH sec) and $E = 8.94$ kcal/mol.

With this consideration and unit ratio of isocyanate to hydroxyl groups, the fractional conversion of BDO hydroxyl groups is given by[14]

$$q_1 = \frac{A_0 kt}{1 + A_0 kt} \tag{3}$$

where A_0 is the initial concentration of isocyanate groups (moles NCO/total mass of the system). Combination of eqs. (1) and (3) and gave the working equation to calculate critical average sequence length of the hard segments at the observed opacity time t_o.

Table I presents a summary of results including conversion and average sequence length at segregation for systems in which pure MDI was used. Similar results for systems using liquid MDI (143L) are presented in Table II. As seen in both Tables, phase separation as measured by the cloud point occurs for all cases at fairly low average sequence length of the hard segments and within experimental error it remains fairly constant. Figure 3 shows how in the case of pure MDI (data of Table I) the time for opacity data at two temperatures agree with the calculated time to achieve $\overline{N}_n = 1.24$.

Thus, we see that for phase separation as measured by light transmittance, there is a critical number average sequence length of hard segments, which dictates the cloud point at all reaction temperatures and MDI/BDO/PPO-PEO starting ratios. The slightly higher values of $\overline{N}_n$ at opacity found for the 143L system may be due to the poorer quality of phase separation attainable with this slightly polyfunctional (ca. 2.2) isocyanate. The weak temperature dependence of the critical average sequence length may be a result of increased miscibility of the two phases at higher temperature and increased mobility of the hard segments (T_g of these segments occurs near 110°C).

Although the cloudiness exhibited by the samples at some point in the reaction

TABLE II
Summary of Light Transmission Results for Systems Using "Liquid MDI," 143L

Temperature (°C)	Molar ratio MDI/BDO/PPO	Segregation time (min)	Fractional conversion	Number average seq. length	
25	5/4/1	32.4	0.49	1.23	
	5/3/2	122.6	0.70	1.42	
	5/2/3	220.0	0.77	1.31	$\bar{x} = 1.32$
55	5/4/1	8.3	0.49	1.24	
	5/3/2	25.3	0.66	1.35	
	5/2/3	107.2	0.86	1.41	$\bar{x} = 1.33$
95	5/4/1	3.4	0.63	1.48	
	5/3/2	11.7	0.80	1.62	
	5/2/3	16.0	0.80	1.35	$\bar{x} = 1.48$
110	5/2/3	16.5	0.87	1.56	

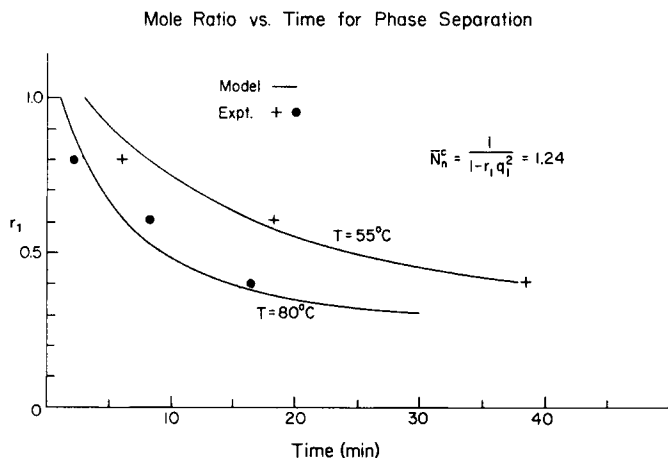Mole Ratio vs. Time for Phase Separation

Fig. 3. Comparison of experimental results with predictions of segregation time when the critical number average sequence length of hard segments is taken as $\overline{N}_n = 1.24$. Data points shown are the observed opacity times for various compositions. The lines are calculations of the time to achieve $\overline{N}_n = 1.24$ for various compositions.

is clearly due to heterogeneous structure, our initial assumption that the cloud point corresponds exactly to the onset of phase demixing has to be tested more rigorously. Domain sizes measured by other techniques such as small-angle x-ray scattering (SAXS) have been reported to be between 3 and 15 nm.[6,18–20] These values are far too low compared to the structure sizes that would be required to obtain effective light scattering, sufficient for the samples to appear opaque. On the other hand, the low end of the above range (3 nm) does correspond to a length of about 1.5 hard segment units.[6]

It is possible that the cloudiness of the sample is associated with the formation of other superstructures such as spherulitic arrangements[6,8] which would provide enough density differences with respect to the other nonspherulitic regions. We are currently conducting a series of SAXS and Fourier-transform infrared experiments to study the phase separation *during* the reaction, from which we expect to get a more accurate picture of the development of segregated structure in polyurethane systems.

Viscosity Rise

The viscosity rise, as obtained from the RMS is shown in Figure 4 for three different temperatures. An interesting result is that although the system under study is basically thermoplastic (crosslinking from ca. 2.2 functional 143L is low), we find a viscosity rise similar to that of a thermoset system. The viscosity rise point is not as sharply defined as the onset of turbidity, however.

We postulate that the increase in viscosity in this system is also caused by the segregation that takes place during the polymerization. The hard domains formed act as suspended particles. As the polymerization proceeds, the suspension of hard domains (with cilia into the soft phase) becomes more concentrated up to the point where the different domains are interconnected. The viscosity then appears to become infinite.

As in the case of the light transmission the time variable can be mapped into
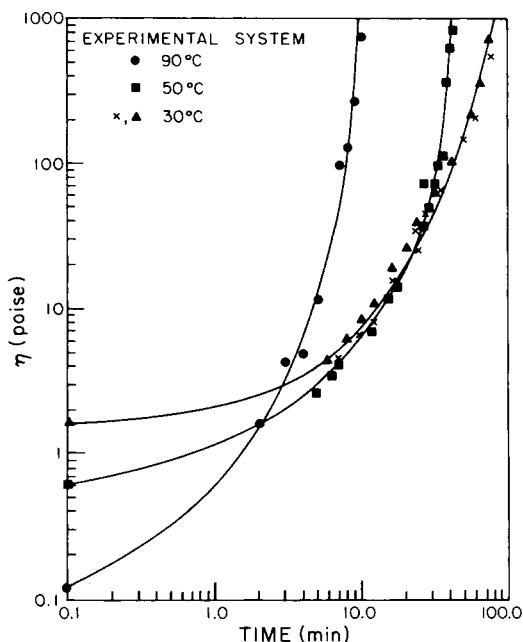
Fig. 4. Viscosity increase vs. time for a polyurethane system (MDI/BDO/PPO-PEO = 5/4/1) at various temperatures.

the conversion domain, using the kinetics of the system. In Figure 5 a plot of the viscosity of the system relative to the initial viscosity η/η_0 versus conversion of BDO hydroxyls q_1 shows a single curve which is independent of the temperature and gives for the stoichiometry studied here a gel point conversion of 0.85. The number average sequence length at this point, calculated from eq. (1), is 3.6. From our previous discussion, this should be the conversion at which the hard domains become interconnected, either through crowding of the domains as in a simple particle suspension or through physical crosslinking via tie chains.

Castro and Macosko[16] have presented some modelling equations for the viscosity rise in some RIM urethanes, and a more detailed analysis of other compositions for the system presented here is in progress. We note here that the viscosity measurement is sensitive to a different aspect of the phase separation during polymerization than the light transmission experiment. Figure 6 shows that the viscosity rise is above that expected from molecular weight growth alone and is observed right from the very beginning of the reaction. This indicates the development of some structures which do not produce turbidity. On the other hand for both turbidity development and viscosity rise there appear to be two distinct, critical conversions for opacity and gelation, respectively.

CONCLUSIONS

This study demonstrates that the phase separation observed in polyurethane systems occurs at early stages in the reaction. There are at least two size scales of phase separated structure and perhaps even a continuum of sizes of phase separated domains formed *during* polymerization. Cooper and co-workers[21] have recently suggested that a continuum of domain sizes exist in bulk polyurethane samples from annealing and melting studies by calorimetry.
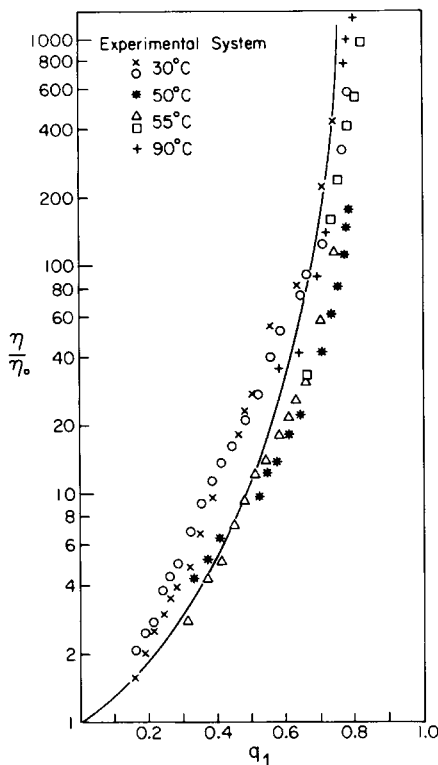
Fig. 5. Relative viscosity vs. fractional conversion of extender hydroxyl groups at various temperatures (system described in Fig. 4).

One distinct size scale is detected optically. These must be of order $10^2\, nm$ and therefore represent aggregates of hard segments, perhaps spherulites[6] or some other crystallite arrangement. If the time which the sample becomes opaque is taken as the onset of this type of segregated structure within the system, we have shown that the number average sequence length of the hard segments at the instant of segregation is fairly constant, and to a large extent, independent of the composition and reaction temperature in the range of 16% to 38% hard segment and for reaction temperatures below the glass transition temperature of the hard segment. Hager et al.[22] have very recently reported a transition observed through calorimetry on polymerizing media, which they attribute to phase separation and which *also occurs at $\overline{N}_n$ = 1.25 to 1.30* over a range of compositions. This is more than coincidence; understanding the correspondence should be a very fruitful activity.

The phase separation during urethane polymerization is also responsible for the sharp increase in viscosity of these systems and apparent gel points occurring before the reaction is completed. Viscosity is sensitive to a different and earlier aspect of the phase separation process.

We continue to study this phenomenon and to extend our studies to temperatures above the glass transition temperature of the hard segment. We feel that phase separation during urethane polymerization may be a key factor not only in determining the final morphology of the segmented polyurethane formed, but also in affecting the molecular characteristics of the material polymerized after
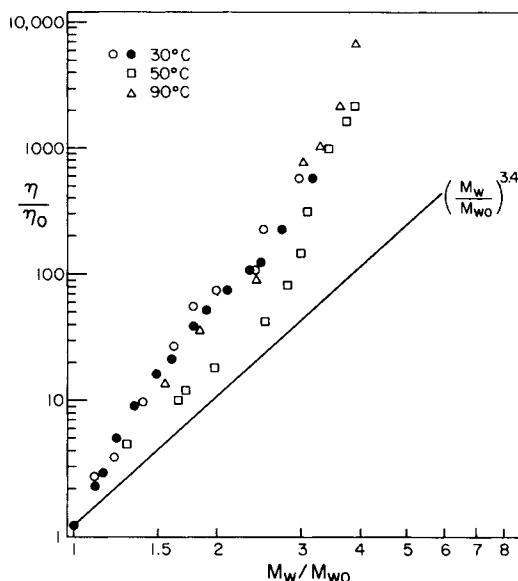
Fig. 6. Data on reduced viscosity vs. molecular weight for a urethane system like that of Figure 4. If molecular weight growth alone were responsible for viscosity rise we would expect η/η_0 to increase with the 3.4 power of (M_w/M_{w0}).

the phase separation point. These effects are likely to be especially important in polymerization processes such as RIM where fairly low, and often spatially inhomogeneous, reaction temperatures are normal.

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