also consistent with the above explanation. **3e** also exists in an ordered conformation in aqueous NaOH on the basis of abnormal optical rotation and CD spectrum. **3e** and **3f** would be new polyamides exhibiting reversible formation of a ordered conformation on changing the basicity of the media.[15] Although the CD spectra of **3d** in DMAc and in aqueous NaOH are not conclusive, **3d** would exist in a very rigid and tight structure that cannot be altered by the basicity of the media.

Acknowledgment. We acknowledge the technical assistance of Junko Umezawa and Kazutoshi Fujioka. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 59850147) from the Ministry of Education, Science and Culture.

References and Notes

(1) Selegny, E. *Optically Active Polymers*; D. Reidel: Dordrecht, 1979.
(2) Corley, L. S.; Vogl, O. *Polym. Bull. (Berlin)* **1980**, *3*, 211.
(3) Hatada, K.; Shimizu, S.; Yuki, H.; Harris, W.; Vogl, O. *Polym. Bull. (Berlin)* 1981, *4*, 179.
(4) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*, 156.
(5) Okamoto, Y.; Suzuki, K.; Yuki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3043.
(6) Okamoto, Y.; Suzuki, K.; Kitayama, T.; Yuki, H.; Kageyama, H.; Miki, K.; Tanada, N.; Kasai, N. *J. Am. Chem. Soc.* **1982**, *104*, 4618.
(7) Okamoto, Y.; Ishikura, M.; Hatada, K.; Yuki, H. *Polym. J. (Tokyo)* **1983**, *15*, 851.
(8) Green, M. M.; Gross, R.; Stassi, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*, 76 and references therein to the earlier literature in this area.
(9) Overberger, C. G.; Wang, D. W. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1153 and references therein.
(10) Hasegawa, M.; Saigo, K.; Katsuki, H.; Yonezawa, N.; Kanoe, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2345.
(11) Saigo, K.; Yonezawa, N.; Sekimoto, K.; Hasegawa, M.; Ueno, K.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1000.
(12) Yonezawa, N.; Kanoe, T.; Saigo, K.; Chen, Y.; Tachibana, K.; Hasegawa, M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 617.
(13) Brown, H. C.; Heim, P. *J. Am. Chem. Soc.* **1964**, *86*, 3566.
(14) Yonezawa, N.; Hasegawa, M. *Bull. Chem. Soc. Jpn.* **1984**, *56*, 367.
(15) Morawetz, H. *Macromolecules in Solution*; Wiley-Intersceince: New York, 1975.

Monte Carlo Simulation Study of the Polymerization of Polyurethane Block Copolymers. 1. Natural Compositional Heterogeneity under Ideal Polymerization Conditions

Thomas A. Speckhard,† **John A. Miller,**† **and Stuart L. Cooper***

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.
Received October 30, 1985

ABSTRACT: The synthesis of polyurethane block copolymers is a complex process involving the condensation polymerization of three monomers in a one-step, two-step, or multistep reaction with the composition and molecular weight distributions of the final polymer influenced by a number of factors including the extent of reaction; relative reactivity, type, and amount of the monomers; and the extent to which various side reactions occur. In order to describe the effects of various reaction parameters on the composition and molecular weight distributions of polyurethane block copolymers, a Monte Carlo simulation has been developed utilizing several simplifying assumptions proposed by Peebles (Peebles, L. H. *Macromolecules* 1974, *7*, 872). The model calculates the molecular weight and composition distributions of the final polymer and simulates fractionation of the polymer based on composition. Using this idealized model, the effects of varying the average degree of polymerization, diisocyanate reactivity ratio, hard-segment content, soft-segment molecular weight distribution, average hard- and soft-segment block length, hard-segment type, and lower limit of the degree of polymerization on the composition and molecular weight distributions of polyurethane block copolymers are determined and discussed.

I. Introduction

Polyurethane block copolymers are usually prepared in a two-step reaction by first reacting a diisocyanate with a hydroxy-terminated polyether or polyester macroglycol. This oligomer is commonly referred to as the soft-segment polyol. The diisocyanate groups are in excess; therefore, the primary product of the first step of the reaction is a diisocyanate-capped soft segment. The reaction products will also include unreacted diisocyanate molecules and some higher molecular weight species produced by linking two or more soft segments through reaction of both ends of a diisocyanate molecule. It is generally assumed that all of the soft-segment hydroxyl groups react, and therefore all product species are isocyanate terminated.[1]

In the second reaction step, the remaining isocyanate functionality is then reacted with a low molecular weight diol or diamine, which is known as the chain extender. Reaction of the chain extender with the free diisocyanate molecules produces hard-segment sequences of various lengths with the average length depending on the stoichiometry of the overall reaction. In the final polymer, the hard and soft segments tend to segregate, due to their incompatibility, and produce a phase-separated morphology of hard-segment-rich and soft-segment-rich phases. This two-phase structure gives rise to the interesting and useful properties of these materials.[2,3]

Normally, the amount of chain extender added in the second step is such that in the final reaction mixture there are an equal number of hydroxyl and isocyanate groups. In some cases, excess isocyanate functionality is used to promote cross-linking by the reaction of active urethane hydrogen atoms (or urea hydrogens if a diamine chain extender is used) to form allophanate (or biuret) linkages. Excess isocyanate is also used because any water present in the system will react with the isocyanate groups, leading to a lower molecular weight in water-poisoned systems that are stoichiometric. The reaction chemistry is further complicated by the fact that the isocyanate groups can

---

† Current address: 3M Research Center, St. Paul, MN 55144.

* Author to whom correspondence should be addressed.

0024-9297/86/2219-1558$01.50/0

self-polymerize under suitable conditions, with the dimer and trimer species being fairly common.[1] Experimental work has indicated that the reactivity of an isocyanate function on a symmetric diisocyanate molecule depends on whether or not the other isocyanate group has reacted.[4,5] Asymmetric diisocyanates also produce different hard-segment-length distributions because of the difference in the individual isocyanate group reactivity. Finally, the reaction to form polyurethane block copolymers can follow pathways different than that described above. For example, all of the reactants can be added simultaneously in a so-called one-step reaction. It is also possible to first react the isocyanate and the chain extender followed by reaction with polyol or the reaction product from the first step of the normal two-step procedure. Multistep synthesis procedures can also be used.[6]

Polyurethane chemistry has been used commercially for many years.[7] However, because of the complexities described above, little attention has been paid to the kinetics of polymerization and the precise composition of the hard and soft segments and the polymer molecules. Interest in these parameters has increased since papers appeared describing the effects of hard- and soft-segment-length distributions on the structure–property relationships of polyurethanes.[6,8–11] The effect of varying sequence distribution in random copolymers is well-known,[12,13] and Frensdorff[14] and Helfand[15] have developed a mathematical approach for predicting the weight or mole fraction of polymer molecules with a given number of sequences greater than a specified length. Sorta and Melis[16] adapted the approach of Frensdorff and Helfand so that the average sequence length and sequence-length distribution could be calculated for poly(ether ester amide) copolymers of finite molecular weight. These materials were synthesized in a one-step condensation reaction analogous to that used to synthesize polyurethanes. The authors noted that the effects of a finite molecular weight on the average sequence length and sequence-length distribution were particularly noticeable below number-average molecular weight ($\bar{M}_n$) of 30 000. Lopez-Serrano et al.[17] have developed a new method for calculating average values of molecular weight, chain-length, and sequence distributions in linear copolymerizations. Their method can be used without the normal simplifying assumptions of equal reactivity and stoichiometry.

Peebles[1,18] has developed a methodology to determine the length distribution of the hard segments in polyurethane block copolymers. To make the problem manageable, Peebles made the following assumptions: (1) The hydroxyl–isocyanate reaction is irreversible. (2) The chain extender is a diol. (3) The reactivity of a symmetrical or nonsymmetrical isocyanate group is independent of molecular weight. (4) The reactivity of one end of a symmetrical diisocyanate monomer depends only on whether the other end of the monomer has reacted. (5) All hydroxyl groups have the same reactivity. (6) No other reactions (such as cross-linking) occur. On the basis of those assumptions, Peebles showed that under stoichiometric conditions and 100% conversion the distribution of hard-segment lengths follows the most probable distribution.

Peebles also studied the effects of degree of conversion (molecular weight), stoichiometry, and the relative reactivity (μ) of the two isocyanate functionalities on a diisocyanate molecule on the average hard-segment length and length distribution. Increasing the molar ratio of isocyanate to polyol under stoichiometric conditions, for example, by using a 6/5/1 ratio of isocyanate to chain extender to polyol in comparison to a 2/1/1 ratio, increases the average hard-segment length and also broadens the hard-segment-length distribution. Increasing molecular weight or conversion also serves to increase the average hard-segment length and broaden the distribution since coupling of shorter hard segments to form long hard segments occurs more frequently as conversion increases. For the case of a symmetrical isocyanate molecule, μ is defined as (k_1/k_2), where k_1 is the rate constant of the first isocyanate group to react and k_2 is the rate constant for the remaining isocyanate group. Increasing μ was found to produce a narrower distribution of hard-segment lengths. Peebles also treated the case of nonsymmetrical diisocyanates where the difference between k_1 and k_2 is due to steric and electronic effects. In this case the effects of sequential reaction were ignored. Changes in μ produced similar trends for both the symmetric and nonsymmetric cases, but the average hard-segment length was shorter and the distribution broader for the nonsymmetrical case with $\mu \geq 1$. For the limiting case where μ approaches infinity, the reaction in the first step of a two-step reaction scheme is carried out perfectly, and only isocyanate-capped polyols and free diisocyanate molecules are present in the reaction mixture. The second step of the reaction will produce a distribution of hard-segment lengths that is relatively narrow but not monodisperse. Finally, Peebles showed that under stoichiometric conditions the products of a one-step reaction with any value of μ are the same as for a two-step reaction with $\mu = 1$. Several authors have subsequently made use of Peebles' work to describe the effects of hard-segment length on the structure–property relationships of polyurethanes.[6,19]

A phenomenon related to that of the effect of a distribution of sequence lengths on copolymer properties is the effect of a distribution of compositions of the molecules on the physical properties of the polymers. A distribution of compositions can arise in several ways and lead to different types of compositional heterogeneity. In the case of random copolymers, the synthesis generally produces molecules rich in the more reactive component in the early stages of the reaction. After the more reactive component is almost depleted, the polymer molecules produced are rich in the other component. From this type of reaction it is theoretically possible to have a distribution of compositions that is independent of molecular weight. In the case of a diblock copolymer the first monomer is usually synthesized by an anionic polymerization that produces an almost monodisperse product. Thus, when the second monomer is polymerized, the overall molecular weight and the composition of the final polymer are directly related. If the second blocks are not monodisperse, the final polymer will consist of molecules that at a given molecular weight will all have the same composition, but the composition varies directly with molecular weight. In the most general case, a copolymer could have a different distribution of compositions at each molecular weight. Skeist[20] has developed a method for calculating the copositional heterogeneity of a random copolymer based on the monomer reactivity ratios, and Nielsen[21] has described some of the effects of compositional heterogeneity in random copolymers on physical properties.

Little attention has been paid to the phenomenon of compositional heterogeneity in polyurethane copolymers, largely because of the complexities of the synthesis procedure noted above as well as the difficulty in obtaining data that adequately describes the heterogeneity of a system. Recently, Xu et al.[22] have reported on the effects of compositional heterogeneity in a series of polybutadiene

(PBD) polyurethanes. These samples were prepared by a two-step bulk reaction; a hydroxy-terminated PBD oligomer was reacted with an isomeric blend of toluene diisocyanate followed by chain extension with butanediol. These materials exhibited two hard-segment glass transition temperatures, low molecular weight, and poor mechanical properties. Xu et al. fractionated the samples into sol and gel fractions in *N*,*N*-dimethylformamide (DMF) at 70 °C. Infrared spectroscopy indicated that the sol fraction had a much higher hard-segment content than the gel fraction. In effect, the sample could be thought of as a blend of two polyurethanes with different stoichiometries. For example, a blend of a material with a 10/9/1 molar ratio of isocyanate to chain extender to polyol with a 2/1/1 molar ratio material will produce a nominal 6/5/1 material with a bimodal hard-segment distribution and compositional heterogeneity.

Chen et al.[23] studied the polymerization of the same PBD polyurethanes and found that early in the second step of the reaction the reactants phase separated to form butanediol-rich regions. The final morphology of the polymer was largely determined by this phase separation during polymerization. The DSC results of Xu et al. showed that the sol and gel fractions exhibited different hard-segment glass transition temperatures that corresponded to the two T_gs observed in the unfractionated material, thereby demonstrating the segregation effect during polymerization on the final polymer. Xu et al. attributed the poor mechanical properties of these materials to the brittle behavior of the hard-segment-rich material and to low overall molecular weight caused by an imbalance in isocyanate and hydroxyl groups in the individual phases of the reaction mixture. Subsequent work on PBD polyurethanes synthesized in solution to reduce reactant incompatibility effects[24] led to higher molecular weights and improved physical properties. In addition, no evidence for compositional heterogeneity was observed. Finally, Xu et al. suggested that reactant incompatibility effects leading to compositional heterogeneity should be common in polyurethanes, especially those polymerized in bulk. These effects were especially evident in their study because of the extreme incompatibility of the reactants. Compositional heterogeneity due to reactant incompatibility has also been noted in polyisobutylene-based polyurethanes,[25] and other researchers have noted the effects of phase separation during a bulk polymerization of polyurethane systems.[26-28]

Although most polyurethane block copolymers do not show obvious signs of compositional heterogeneity such as two hard-segment T_gs, consideration of the synthesis procedure even under idealized conditions indicates that because of their finite molecular weight, individual polyurethane molecules will have different compositions. For example, at low conversions many low molecular weight species will be present, and it is obvious that the composition of an isocyanate-capped polyol is not the same as that of an isocyanate-capped chain extender. Only at 100% conversion will the sample be homogeneous and then because only one molecule will exist. The compositional heterogeneity that results from the finite molecular weight of the polymer will be termed the "natural heterogeneity".

The question then arises as to what extent can the compositional heterogeneity observed in materials such as the PBD polyurethanes be attributed to the natural heterogeneity associated with finite molecular weight. If the natural heterogeneity can be determined from a knowledge of the synthesis conditions and the reaction conversion, it would then be possible to evaluate the observed compositional heterogeneity for excess heterogeneity that must be attributed to other effects. In this paper, we report the results of a Monte Carlo simulation of the natural heterogeneity caused by finite molecular weight in polyurethane block copolymers using an idealized model that incorporates the same assumptions made by Peebles. Thus, the distribution of hard-segment lengths is assumed to follow the most probable distribution. Additionally, the degree of polymerization in terms of segments is assumed to follow the most probable distribution. In the second and third papers[29,30] of this series, we utilize different models to try to simulate the effects of phase separation during reaction and other factors that could give rise to "excess" heterogeneity. These models also give rise to situations where the hard-segment-length distribution is not the most probable distribution. Finally, in the fourth[31] paper, the various models are used to evaluate the experimental results of Xu et al. on PBD polyurethanes. All of the models simulate the synthesis of polymer chains and fractionation of a polymer sample based on composition.

II. Model Description

As a starting point for our idealized model of the polyurethane synthesis, we make the same six assumptions made by Peebles (noted above). A further restriction is that we will only consider the case of symmetrical diisocyanates so that the analytical expressions developed by Peebles to determine the hard-segment-length distribution can be used. In Peebles' treatment the nonsymmetrical case is not described analytically but gives rise to similar trends with changes in μ. Also, only stoichiometric systems are examined. (Nonstoichiometric cases will be treated in the third paper.[30]) This model is referred to as the single-phase ideal reaction model.

The simulation of the polymerization begins by selection of the molar ratio of the reactants, the type of diisocyanate and chain extender used, and the type of soft segment used and its molecular weight. The reactivity ratio (μ) of the diisocyanate species can also be varied. Peebles[1] has listed experimentally determined[4,5] μ values. For example, MDI has a value of $\mu \cong 3$ while 2,4-toluene diisocyanate (TDI) has a value of $\mu \sim 12$–25. The values of μ are dependent on the conditions of the experiment such as solvent and catalyst type, temperature, and specific type of alcohol reacting. Typically, methylenebis(*p*-phenyl isocyanate) (MDI) and butanediol were used for the diisocyanate and the chain extender for the simulation. The molecular weight distribution of the soft-segment polyol can be specified as well. It should be noted that in this model a soft segment is defined as the portion of the copolymer arising from reacted polyol groups and does not include any reacted diisocyanate units. Thus, the soft-segment molecular weight and polyol molecular weight distributions are directly related. For 1000 mol wt poly(tetramethylene oxide) (PTMO) a distribution based on HPLC data ($\bar{M}_n = 1008$) was normally used.[32] More generally, a Schulz distribution[33] for the soft segments with $\bar{M}_n$ and $\bar{M}_w$ as parameters could be used ($\bar{M}_w$ is the weight-average molecular weight). The Schulz distribution was calculated with discrete values based on the soft-segment-monomer molecular weight. The soft-segment size can also be fixed at a constant value, thus creating a monodisperse soft-segment molecular weight distribution.

The hard-segment-length distribution was then calculated following Peebles.[1,18] A monodisperse hard-segment-length distribution can also be used. In this model the hard-segment length is defined by the number of diisocyanate species that it contains. Thus, a single diisocyanate species between two polyols is considered to be a hard segment. No chain extender is present in such a segment. The number of hard segments 1 unit long in the final polymer (N_1) is given by the number of diisocyanate units that have both isocyanate groups reacted in the first step of the reaction. If both isocyanate groups of a diisocyanate molecule react during the first step, it is called an internal diisocyanate residue, and the mole fraction of these species (X_1^{int}) can be calculated by using the results of Peebles[1,18]

$$X_1^{\text{int}} = 2B_1 + X_1^0 - A_1 \qquad (1)$$

where A_1 and B_1 are the initial number of moles of diisocyanate and polyol, respectively, and X_1^0 is the residual number of moles of diisocyanate species that has not reacted at all. This quantity is the positive root of the relation[1]

$$\mu(X_1^0/A_1)^{1/2\mu} + (\mu - 1)X_1^0/A_1 = (2\mu - 1)(A_1 - B_1)/A_1 \qquad (2)$$

Peebles[1,18] has shown that at 100% conversion the distribution of hard segments follows the most probable distribution. In that case the number of hard segments of any length is given by

$$N_i = N_2 p^{i-1} \qquad (3)$$

where N_2 is the mole fraction of hard segments with two isocyanate species present and p is a constant for a given set of reaction conditions. Since all of the mole fractions must add up to unity, we can derive

$$\sum_{i=2}^{\infty} N_i = 1 - N_1 \qquad (4)$$

and since $N_1 = X_1^{\text{int}}$, it can be shown that for the stoichiometric case

$$p = X_1^0/C_1 \qquad (5)$$

where C_1 is the initial concentration of the chain extender. The distribution of the hard segments can then be calculated and used in the simulation. The assumption that the hard-segment distribution follows a most probable distribution will introduce errors when the conversion is less than 100%. In particular, the average hard-segment length will be too high, and the model will predict too many long hard-segment lengths. However, the error introduced by this assumption should be small at conversions over 90%[1] and should not affect the major trends in the data generated by using the Monte Carlo simulation.

The next step in the program is to choose an average degree of polymerization. In this model the degree of polymerization (D_p) is defined in terms of the number of hard and soft segments and so can be referred to as the block degree of polymerization (BD_p). For example, a BD_p of 30 indicates a polymer containing 15 hard and 15 soft segments. It is assumed that the block degree of polymerization will follow a most probable distribution; Flory[34] has shown this to be true for a condensation polymerization for which the D_p is defined in terms of monomer species. In the present case the BD_p distribution should closely approximate a most probable distribution since the hard and soft segments can be considered as monomers.

At this point the model is ready to make use of a Monte Carlo method.[35,36] Monte Carlo methods have been used to simulate a number of situations of interest in polymer science including condensation polymerizations.[37] In general, Monte Carlo methods involve making a large number of random choices among potential outcomes to approximate an average property or property distribution of interest. In this model, a hypothetical polymer sample that has approximately the same molecular weight and composition characteristics as a real polyurethane material polymerized under the given conditions is created by making a large number of random choices from the appropriate distributions as detailed below. In should be noted that this model uses an infinite pool approach; that is, when a particular item is selected from a distribution (or pool), it is in effect replaced and the pool is not diminished.

The actual simulation of the synthesis proceeds in the following manner. A block degree of polymerization (BD_p) is selected at random, as is the identity of the first segment, hard or soft. Segments are then selected in an alternating fashion so as to produce a block copolymer, with the length (molecular weight) of each segment chosen by using the appropriate distribution of segment lengths. When the number of segments in the chain matches the previously selected BD_p, the chain is considered to be finished and the "reaction" stops. The process is repeated until the desired number of chains (typically 15000) has been generated. At the end of the simulation, the average composition of the sample, the number- and weight-average molecular weights, $\bar{M}_w/\bar{M}_n$, and the degree of conversion for the whole sample can be calculated. Histograms of BD_p vs. composition, molecular weight vs. composition, and BD_p vs. molecular weight can also be produced.

The second part of the modeling procedure involves a simulation of a solvent fractionation of the synthesized sample. Although the fractionation process probably depends on both the molecular weight and composition, in this step it is assumed that fractionation occurs only on the basis of composition. To simulate a fractionation where the soft-segment-rich fraction comprises 30% of the total weight of the polymer chains, the program starts with the lowest hard-segment-content chains and sums the total weight fraction of the chains until a value of 0.3 is reached. The average composition, $\bar{M}_n$, and $\bar{M}_w$ of the fraction are then calculated. Similar quantities are also calculated for the remaining hard-segment-rich fraction. The program also allows for the calculation of multiple fractionation points (i.e., independent summing to 0.3, 0.4, 0.5, etc. weight fraction) and calculates all of the appropriate parameters. These fractions are all calculated starting with the lowest hard-segment-content species. Finally, plots of cumulative and intermediate weight fraction vs. composition can be generated.

This model is applicable to ideal one- and two-step homogeneous solution polymerizations. The one-step polymerization can be modeled by using a diisocyanate reactivity ratio of unity. The two-step reaction is the standard case for this model. Reactions in the bulk state that follow the ideal reaction conditions can also be modeled. Any nonideality in the reaction parameters such as premature phase separation or differences in reactivity between the polyol and chain extender will preclude the use of this model. The development of more sophisticated models to simulate these effects, which contribute to excess compositional heterogeneity in polyurethanes, will be the topic of the second and third papers in this series.[29,30]

The major errors involved in the use of the computer to implement the model involve the normal small errors associated with using a finite number of chains and round-off errors, and approximating the BD_p, and hard- and soft-segment-length distributions by finite distribution arrays. Some additional error is assumed in defining the degree of polymerization of the whole chain by the block degree of polymerization, but this error is small at high conversions. Also, the hard-segment-length distribution

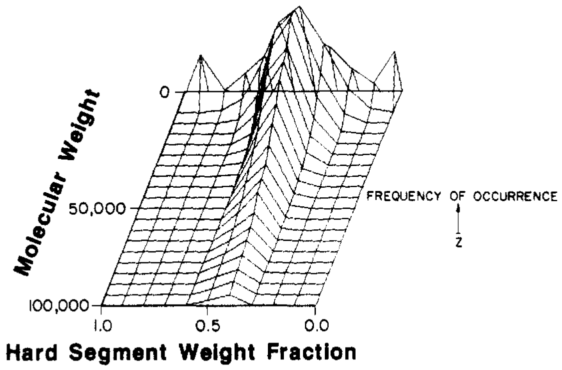

Figure 1. Three-dimensional histogram of frequency of occurrence (z axis) vs. molecular weight (y axis) and hard-segment weight fraction (x axis) for the base-line case with $\overline{\mathrm{BD}}_p$ = 30.

is calculated on the basis of total conversion of the reactants. This leads to a small error in the hard-segment-size distribution, but affects the total molecular parameters very little. Prior to the fractionation procedure, molecular weights are rounded off to the nearest value of 10 and compositions are rounded off to the nearest 0.001% value. The computer program was written in FORTRAN-77 and run on a Digital Equipment Corp. VAX-11/785 minicomputer located in the Department of Chemical Engineering at the University of Wisconsin—Madison.

III. Results and Discussion

To allow for comparison of the effects of varying synthetic parameters on the average composition, composition distribution, average molecular weights, and molecular weight distribution of polyurethane block copolymers, a control or base case was chosen with the following standard parameters: 3/2/1 molar ratio of MDI/BD/PTMO-1000(H), diisocyanate reactivity ratio (μ) of 3, average block degree of polymerization (BD$_p$) of 30, minimum BD$_p$ of 1 (low end cut off), maximum BD$_p$ of 1500, and 15000 chains produced in the simulation. The (H) indicates that the HPLC data ($\bar{M}_n$ = 1008) were used for the soft-segment molecular weight distribution. A value of μ = 3 for the base-line case was chosen on the basis of the value obtained by Ferstandig and Scherrer[4] and Brock.[5] Recent work by Miller et al.[6] suggests that μ is around 1.5 for the reaction of MDI with PTMO. The base-line parameters resulted in a hypothetical material with an average hard-segment content of 48.1 wt %, $\bar{M}_n$ = 28520, $\bar{M}_w/\bar{M}_n$ = 1.952, and a conversion based on monomer units of 0.9887. The effect of varying the number of chains produced in the simulation gave rise to only small random differences on the order of 0.2% in average hard-segment content, 0.1% in fractional compositions, 100 in $\bar{M}_n$, and 0.01 in $\bar{M}_w/\bar{M}_n$ when more than 5000 chains were produced.

In Figure 1 the molecular weight vs. composition data are plotted as a three-dimensional histogram for the base system. The x–y plane is a grid of molecular weight and composition values, while the z axis represents the number of chains in each sector of the grid. As expected, as the molecular weight (or BD$_p$) increases, the composition distribution becomes more narrow. In general, the composition distribution varies smoothly about the average composition; the "bumps" at low molecular weight and low and high hard-segment contents are due to 1-unit-long hard and soft segments. The plot is constructed so that all of the chains whose composition and molecular weight values fall between two lines on the histogram are represented at the lower value of the two lines. Figure 2 displays a plot of the intermediate weight fraction vs. composition data for the base material along with data for an ideal sample with monodisperse hard and soft segments. The x axis in Figures 2, 3, and 6 is the cumulative weight fraction of chains in ascending order of hard-segment composition. As the x value increases, the chains within an x interval possess a higher average hard-segment content than chains in previous x intervals. The y axis is a measure of this change and is the average fraction of hard-segment material in the chains within the specific x interval. This quantity is called the specific hard-segment weight fraction. Since a compositionally homogeneous sample would exhibit a horizontal line at the average composition value, these data clearly indicate the existence of compositional heterogeneity in the base material and to a lesser extent in the ideal sample. In particular, the soft- and hard-segment-rich fractions at the extremes of the curve for the base material possess compositions that differ by as much as 25 wt % hard segment from the overall average composition. The slight compositional heterogeneity of the ideal sample with monodisperse hard and soft segments is due to chains with odd BD$_p$ values that cannot contain an equal number of hard and soft segments. Using the base material as a standard, we have systematically investigated the effects of varying the model parameters on the composition and molecular weight distributions.

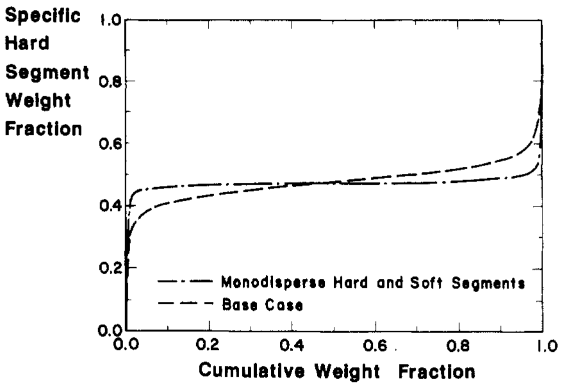

Figure 2. Specific hard-segment weight fraction vs. cumulative weight fraction for the base-line case and a monodisperse hard- and soft-segment material.

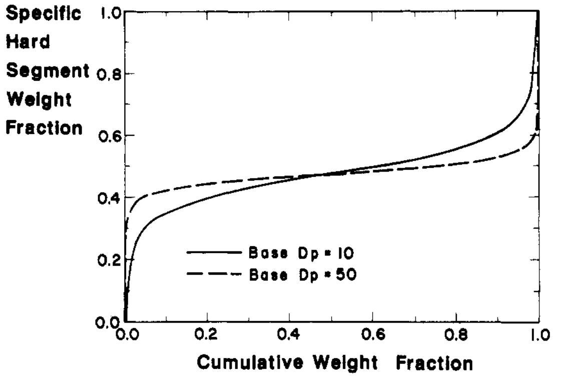

Figure 3. Specific hard-segment weight fraction vs. cumulative weight fraction for the base-line case with different $\overline{\mathrm{BD}}_p$ values.

Decreasing the average BD$_p$ ($\overline{\mathrm{BD}}_p$) would be expected to increase compositional heterogeneity. The results in Table I and Figures 1 and 3–5 show that this trend does occur. The data in Tables I–VIII contain fractional composition data, which can be related to the data in Figures 2, 3, and 6. The fractional compositions in the tables are cumulative average values up to a certain cumulative weight fraction, whereas the figures are specific compositions at certain cumulative weight fraction intervals. Table I summarizes the average composition of the whole

Table I
Effects of Varying the Block Degree of Polymerization on the Molecular Weight and Composition Distributions[a]

$\overline{\mathrm{BD}}_p$	convn	ave composition	fractnl composition 0.1	fractnl composition 0.5	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{N}_w/\bar{N}_n$
			$\mu = 3$				
5	0.9323	47.8	17.5	35.6	4790	1.878	1.800
10	0.9656	48.0	27.7	39.8	9380	1.919	1.900
20	0.9831	48.0	34.1	42.5	19090	1.950	1.950
30	0.9887	48.1	36.9	43.6	28520	1.952	1.967
50	0.9932	48.1	39.6	44.7	47730	1.927	1.980
100	0.9966	47.9	40.8	45.3	96061	1.895	1.990
			$\mu = 1$				
10	0.9655	48.0	24.8	38.6	9380	1.933	1.900
50	0.9932	48.1	38.2	44.1	47710	1.929	1.980

[a] 3/2/1 MDI/BD/PTMO-1000(H).

Table II
Effects of Varying μ on the Molecular Weight and Composition Distributions[a]

μ	convn	ave composition	fractnl composition 0.1	fractnl composition 0.5	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	0.9887	48.1	35.0	42.8	25510	1.959
3	0.9887	48.1	36.9	43.6	28520	1.952
10	0.9887	48.1	37.8	43.9	28520	1.951
100	0.9887	48.1	38.1	44.0	28520	1.950
mono[b]	0.9887	48.1	40.2	44.9	28550	1.944

[a] $\overline{\mathrm{BD}}_p = 30$, 3/2/1 MDI/BD/PTMO-1000(H). [b] Monodisperse hard segments.

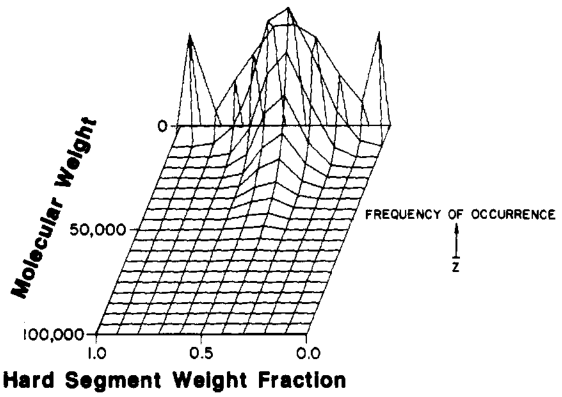

Figure 4. Three-dimension histogram of frequency of occurrence (z axis) vs. molecular weight (y axis) and hard-segment weight fraction (x axis) for the base-line case with $\overline{\mathrm{BD}}_p = 10$.

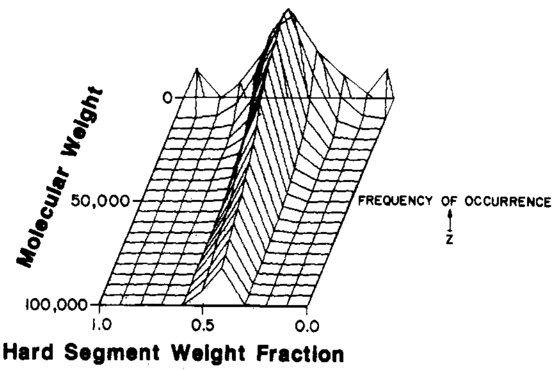

Figure 5. Three-dimensional histogram of frequency of occurrence (z axis) vs. molecular weight (y axis) and hard-segment weight fraction (x axis) for the base-line case with $\overline{\mathrm{BD}}_p = 50$.

sample, the average composition of the 0.1 and 0.5 weight fractions of the samples that are richest in soft-segment content, $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, $\bar{N}_w/\bar{N}_n$, and the reaction conversion for cases with various $\overline{\mathrm{BD}}_p$ values. $\bar{N}_w$ is the weight-average number of blocks per polymer chain, and $\bar{N}_n$ is the corresponding number-average value. The remaining parameters are fixed at the same value as in the reference case. The data in Table I indicate that the fractional compositions at both 0.1 and 0.5 soft-segment-rich weight fraction decrease markedly as $\overline{\mathrm{BD}}_p$ decreases. Figure 3 displays the intermediate weight fraction vs. composition curves for the samples with $\mu = 3$ and $\overline{\mathrm{BD}}_p = 10$ and 50. The data clearly show that the $\overline{\mathrm{BD}}_p = 10$ sample is more compositionally heterogeneous, as do the molecular weight vs. composition histograms pictured in Figures 1, 4, and 5. Figures 4 and 5 are similar to Figure 1, the only difference being the $\overline{\mathrm{BD}}_p$, which is 10 for Figure 4 and 50 for Figure 5.

The data in Table I also indicate that the molecular weight and conversion increase with increasing $\overline{\mathrm{BD}}_p$ as expected. The molecular weight distribution as measured by $\bar{M}_w/\bar{M}_n$, however, displays more complex behavior. $\bar{M}_w/\bar{M}_n$ would be expected to increase with increasing $\overline{\mathrm{BD}}_p$, a trend that is observed for values of $\overline{\mathrm{BD}}_p$ up to $\overline{\mathrm{BD}}_p = 30$. The last column in Table I shows the ratio of the weight-average ($\bar{N}_w$) and number-average ($\bar{N}_n$) segment lengths based on hard and soft segments (for the base system with $\overline{\mathrm{BD}}_p = 30$, $\bar{N}_n = 30$, and $\bar{N}_w = 59$). These values follow the analytical expression given by Flory,[34] which yields an asymptotic value of 2 for the value of $\bar{N}_w/\bar{N}_n$ as $\overline{\mathrm{BD}}_p$ increases. Comparing the $\bar{M}_w/\bar{M}_n$ values (which for a single monomer condensation reaction should be equivalent to the $\bar{N}_w/\bar{N}_n$ values) shows that at low $\overline{\mathrm{BD}}_p$ values the $\bar{M}_w/\bar{M}_n$ values are higher than expected while at high $\overline{\mathrm{BD}}_p$ the $\bar{M}_w/\bar{M}_n$ values are lower than expected. This behavior is the result of two competing effects. The fact that the "monomers", in this case the hard and soft segments, do not have the same "monomer" molecular weight leads to an increase in $\bar{M}_w/\bar{M}_n$ that is particularly noticeable at low $\overline{\mathrm{BD}}_p$ values and which decreases as $\overline{\mathrm{BD}}_p$ increases. In opposition to this effect is the fact that a finite array is used to represent the $\overline{\mathrm{BD}}_p$ distribution, which eliminates a few very high molecular weight chains from the distribution and results in a lower value of

Table III
Effects of Varying Average Hard-Segment Content on the Molecular Weight and Composition Distributions[a]

A	μ	$\overline{\mathrm{BD}}_\mathrm{p}$	convn	ave composition	ave fractnl composition 0.1	ave fractnl composition 0.5	$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$
				A. Constant $\overline{\mathrm{BD}}_\mathrm{p}$				
2	1	30	0.9830	36.9	11.1	4.6	23 510	1.954
2	3	30	0.9830	37.0	9.2	3.8	23 520	1.950
2	10	30	0.9831	37.0	8.2	3.4	23 530	1.948
3	1	30	0.9887	48.1	13.1	5.3	28 510	1.956
3	3	30	0.9887	48.1	11.2	4.5	28 520	1.952
3	10	30	0.9887	48.1	10.3	4.2	28 520	1.951
5	1	30	0.9932	61.5	13.4	5.4	38 490	1.967
5	3	30	0.9932	61.5	12.1	4.7	38 520	1.960
5	10	30	0.9932	61.5	11.5	4.5	38 530	1.957
				B. Constant Conversion				
2	3	45.15	0.9887	37.0	7.4	3.1	35 270	1.960
5	3	18.07	0.9887	61.4	16.1	6.1	23 240	1.942

[a] $A/(A-1)/1$, MDI/BD/PTMO-1000(H).

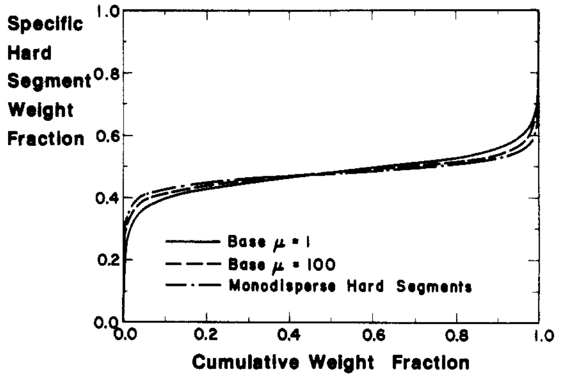

Figure 6. Specific hard-segment weight fraction vs. cumulative weight fraction for the base-line case with $\mu = 1$ and 100 and with monodisperse hard segments.

$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$. This latter effect naturally increases as $\overline{\mathrm{BD}}_\mathrm{p}$ increases. Thus $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ is somewhat lower than expected at high $\overline{\mathrm{BD}}_\mathrm{p}$.

The effects of varying μ can be discerned from the data displayed in Table II and Figure 6. The data in Table II show that the average composition is not markedly influenced by changes in μ. However, the fractional composition data exhibit relatively large changes as μ is varied. As μ increases, the fractional compositions increase, indicating that the sample is becoming more compositionally homogeneous. This behavior would be expected since increasing μ leads to a narrower distribution of the hard-segment lengths.[1,18] In Figure 6 the intermediate weight fraction vs. composition data are plotted for the base system with $\mu = 1$ and 100 and for the sample with monodisperse hard segments. The data clearly show that the sample with $\mu = 1$ is more compositionally heterogeneous than the sample with $\mu = 100$. However, comparing the data for $\mu = 100$ and for the sample with monodisperse hard segments indicates that even with $\mu = 100$ there is still an appreciable contribution of the hard-segment-length distribution to compositional heterogeneity. Narrowing the hard-segment-length distribution should also cause the molecular weight distribution to become more narrow. The values of $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ in Table I (and all other cases studied) support this, although the size of the decrease of $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ with increasing μ is small.

The entries in Table I with $\mu = 1$ allow for investigation of the effect of varying μ at different $\overline{\mathrm{BD}}_\mathrm{p}$ values. Comparing the results for $\mu = 1$ at $\overline{\mathrm{BD}}_\mathrm{p} = 10$ and 50 with the results for $\mu = 3$ at the same $\overline{\mathrm{BD}}_\mathrm{p}$ values shows that as $\overline{\mathrm{BD}}_\mathrm{p}$ increases, the effect of increasing μ, which will narrow the composition distribution, decreases. In general, the effect of varying μ on the breadth of the composition distribution decreases when the composition distribution becomes more narrow due to the effects of other parameters.

The effects of varying the hard-segment content on the composition distribution are not as easy to distinguish as the effects of varying μ and $\overline{\mathrm{BD}}_\mathrm{p}$ because varying the hard-segment content obviously changes the average composition of the sample. Furthermore, at constant $\overline{\mathrm{BD}}_\mathrm{p}$, increasing hard-segment content results in increased conversion and molecular weight. On the basis of the work of Peebles, which indicated that the hard-segment-length distribution becomes broader as the average hard-segment content increases, the composition and molecular weight distribution would also be expected to broaden with increasing hard-segment content. Comparing data in Table IIIA at constant μ shows that as the number of moles of diisocyanate (A) increases from 2 to 5 (since the standard system is stoichiometric this indicates 2/1/1 and 5/4/1 mole ratios) the composition distribution becomes broader as measured by the differences between the average and various fractional compositions.

To examine the effects of increasing the number of moles of diisocyanate (A) at a constant conversion, $\overline{\mathrm{BD}}_\mathrm{p}$ and A were varied from the base case so as to keep the conversion constant. The results of these simulations are summarized in Table IIIB. These data indicate that the expected trend of broadening composition distribution with increasing hard-segment content is observed. In this case, the $\overline{\mathrm{BD}}_\mathrm{p}$ values are decreasing with increasing A and should partially account for the observed trends. However, comparing values at constant conversion does not result in the expected trend of increasing $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ with increasing A values. It should be noted that the expected trend of increasing $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ was observed for the data at constant $\overline{\mathrm{BD}}_\mathrm{p}$ in Table IIIA. The lack of the expected trend in $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ with increasing A at constant conversion is attributable to the differences in $\overline{\mathrm{BD}}_\mathrm{p}$. As noted above, increasing $\overline{\mathrm{BD}}_\mathrm{p}$ leads to increasing $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$; thus the $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ data in Table IIIB with decreasing $\overline{\mathrm{BD}}_\mathrm{p}$ but with increasing A reflect the competition between the two effects. Finally, an examination of the data in Table IIIA at different μ values indicates that the same trends with increasing μ are observed as were previously discussed, but the magnitude of the effects decreases as A increases.

The effect of varying A at different $\overline{\mathrm{BD}}_\mathrm{p}$ values can be

Table IV
Effects of Varying Hard-Segment Content (A) on the Molecular Weight and Composition Distributions at Different $\overline{\mathrm{BD}}_\mathrm{p}$ Values[a]

A	$\overline{\mathrm{BD}}_\mathrm{p}$	convn	ave composition	ave fractnl composition 0.1	0.5	fractnl composition diff	ratio[b]	$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$
				A. Constant $\overline{\mathrm{BD}}_\mathrm{p}$					
2	10	0.9484	36.9	16.7	7.0	9.7	1.45	7740	1.915
5	10	0.9793	61.5	22.5	8.4	14.1		12656	1.938
2	50	0.9899	36.9	7.0	2.9	4.1	1.34	39380	1.925
5	50	0.9959	61.4	9.7	3.6	5.5		64370	1.930
				B. Constant Conversion					
2	14.7	0.9656	36.9	13.5	5.6	7.9	2.44	11600	1.951
5	5.9	0.9655	61.5	30.6	11.3	19.3		7610	1.892

[a] $A/(A-1)/1$, MDI/BD/PTMO-1000(H), $\mu = 3$. [b] Defined as the ratio of the fractional composition difference of the trial for $A = 5$ to that for the trial when $A = 2$.

Table V
Effects of Varying Soft-Segment Molecular Weight Distribution on the Molecular Weight and Composition Distributions[a]

soft-segment distrbn ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$)	ave composition	fractnl composition 0.1	0.5	fractnl M_n (0.1)	$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$
HPLC (1.45)	48.1	36.9	43.6	14020	28520	1.952
fixed (1.0)	47.9	39.4	44.6	12180	28600	1.945
Schulz (1.2)	48.1	38.1	44.2	13200	28530	1.948
Schulz (1.5)	48.1	36.6	43.5	14630	28490	1.953
Schulz (1.7)	48.0	35.7	43.0	14710	28570	1.957

[a] $\overline{\mathrm{BD}}_\mathrm{p} = 30$, $\mu = 3$, 3/2/1 MDI/BD/PTMO-1000.

Table VI
Effects of Varying Soft- and Hard-Segment-Block Length on the Molecular Weight and Composition Distributions[a]

A	soft-segment distrbn ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$)	soft segment, $\bar{M}_\mathrm{n}$	ave composition	ave fractnl composition 0.1	0.5	$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$
3	Schulz (1.5)	1008	48.1	11.5	4.6	28490	1.953
6	Schulz (1.5)	2125	48.0	12.9	5.2	59660	1.957
3[b]	Schulz (1.5)	1008	48.2	8.4	3.4	28520	1.945
6[b]	Schulz (1.5)	2125	48.2	8.4	3.4	59830	1.957
3	fixed (1.0)	1008	47.9	8.5	3.3	28600	1.945
6	fixed (1.0)	2125	48.1	10.4	4.0	59490	1.949

[a] $A/(A-1)/1$ MDI/BD/PTMO, $\overline{\mathrm{BD}}_\mathrm{p} = 30$, $\mu = 3$. [b] Monodisperse hard segments.

discerned from the data in Table IVA,B. At any particular $\overline{\mathrm{BD}}_\mathrm{p}$ value the effect of varying A follows the same trends discussed previously, while at any particular A value the effect of varying $\overline{\mathrm{BD}}_\mathrm{p}$ also follows trends noted in Table I. A measure of the effect of varying A at different $\overline{\mathrm{BD}}_\mathrm{p}$ values is given in Table IVA, which lists the difference in the fractional compositions for the 0.1 and 0.5 soft-segment-rich weight fractions for the 5/4/1 case divided by the difference in the fractional compositions at 0.1 and 0.5 for the 2/1/1 case for several different $\overline{\mathrm{BD}}_\mathrm{p}$ values. At $\overline{\mathrm{BD}}_\mathrm{p} = 10$ this quantity is equal to 1.45, while at a $\overline{\mathrm{BD}}_\mathrm{p}$ of 50 this ratio is 1.35, which suggests that the effect of increasing A is lessened as $\overline{\mathrm{BD}}_\mathrm{p}$ increases. Similarly, the $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ data in Table IVA suggest that the effect of increasing A, which is to broaden the molecular weight distribution, is also reduced as $\overline{\mathrm{BD}}_\mathrm{p}$ increases. The effects of varying A (Table IVB) on the composition distribution at comparable conversion values are also decreased as the conversion increases. However, as noted previously, the magnitude of the effects of varying the average number of diisocyanate species in the hard segments (A) at constant conversion is larger than the effects of varying A at constant $\overline{\mathrm{BD}}_\mathrm{p}$. The effect of increasing A at constant conversion on the value of $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ is again complicated by the change in $\overline{\mathrm{BD}}_\mathrm{p}$ values.

Tables V and VI present data showing the effects of varying the soft-segment molecular weight distribution and the hard- and soft-segment-block length on the composition and molecular weight distribution of the sample. As expected, the data in Table V indicate that broadening the soft-segment molecular weight distribution broadens both the composition and molecular weight distributions. The data in Table V also indicate that the HPLC data used in the base system can be roughly approximated by a Schulz distribution with $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} = 1.5$. This is in excellent agreement with the reported value of 1.45 for the PTMO oligomer on which the HPLC experiment was performed.[32] The effects of increasing the hard- and soft-segment-block lengths can be seen from the data in Table VI. The 6/5/1-2125 samples have approximately the same hard-segment content but roughly twice the average hard- and soft-segment-block lengths as the standard 3/2/1-1000 samples. Comparing the first two entries in Table VI shows the effects of doubling block lengths when there is a distribution of both hard- and soft-segment lengths. In this case the longer hard-block lengths also have broader distributions, and thus the whole polymer has a broader composition and molecular weight distribution. If the effect of the hard-segment-length distribution is removed by making the hard segments monodisperse (second pair of entries in Table VI), the data exhibit no discernible effect of doubling the soft-block length on the composition

Table VII
Effects of Using Different Hard-Segment Types on the Molecular Weight and Composition Distributions[a]

					fractnl composition			
hard-segment type	A	$\overline{BD}_p$	convn	ave composition	0.1	0.5	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
MDI/BD	3	30	0.9887	48.1	36.9	43.6	28 520	1.952
TDI/ED	3.24	30	0.9920	48.1	36.2	43.3	28 520	1.954
TDI/ED	3.24	21	0.9887	48.0	33.7	42.3	20 320	1.945

[a] $A/(A - 1)/1$ PTMO-1000(H), $\mu = 3$.

Table VIII
Effects of Cutting Off the $\overline{BD}_p$ Distribution on the Low End on the Molecular Weight and Composition Distributions[a]

				fractnl composition					
low end cutoff	$\overline{BD}_p$ after cutoff	convn	ave composition	0.1	0.5	fractnl M_n (0.1)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{N}_w/\bar{N}_n$
1	30	0.9887	48.1	36.9	43.6	14 020	28 520	1.952	1.967
2	31	0.9891	48.0	37.0	43.6	14 760	29 580	1.904	1.905
5	34	0.9897	48.0	37.3	43.6	18 240	31 910	1.739	1.753
10	39	0.9914	47.9	38.2	43.8	23 840	37 650	1.565	1.572

[a] 3/2/1 MDI/BD/PTMO-1000(H), $\mu = 3$, $\overline{BD}_p = 30$ (before cutoff).

and molecular weight distributions. This is not surprising since doubling the average value of a Schulz distribution does not broaden the distribution. Alternately, if the soft segments are monodisperse, the composition and molecular weight distributions do become broader with a doubling of the hard-block length, as is seen in the third pair of entries in Table VI. Again this is not a surprising result since the hard segments more or less follow a most probable size distribution. Doubling the average size in a most probable distribution will broaden the distribution. Finally, when both the hard and soft segments are monodisperse, the composition distribution and molecular weight distribution are totally unaffected by changes in the individual block length, as expected.

The effects of using different hard-segment types can be seen in Table VII. If toluene diisocyante (TDI)/ethylenediamine (ED) based hard segments are used instead of MDI/BD, a larger number of TDI species will be needed in an average hard segment to achieve the same hard-segment weight fraction because TDI has a lower molecular weight than MDI and thus will possess a broader hard-segment distribution. This in turn will lead to a broader composition and molecular weight distribution. These effects can be observed in the data listed in Table VII at equivalent values of $\overline{BD}_p$. At constant conversion, the composition distribution is broadened but the molecular weight distribution is narrower due to the difference in $\overline{BD}_p$ values. As seen before, the magnitude of the composition broadening is larger at constant conversion. These results are independent of the overall rate of reaction, which is higher in the TDI/ED system compared to the MDI/BD system. The results only assume that no further reaction occurs. The rate of reaction of the diamine chain extender is more rapid than the reaction rate of the polyol species, which does not make a difference in the modeling of a two-step reaction. It will make a difference in a single-step reaction, and this effect will be studied in the third paper in this series.[30]

The effect of lopping off the low end of the BD_p distribution is of interest because this may actually occur in some synthetic procedures. For example, if the reaction is carried out in solution followed by precipitation into a nonsolvent, it is likely that some low molecular weight species do not precipitate. The effects of cutting off the low end of the BD_p distribution are shown in Table VIII. As expected, both the composition and molecular weight distributions become more narrow as more of the distribution is cut off. The effect on the molecular weight distribution is quite large compared to the effects of the other parameters in this study and is also reflected in the large changes in the $\bar{M}_n$ of the 0.1 soft-segment-rich weight fraction and the $\bar{M}_n$ of the whole sample. The sample conversion also increases as the low BD_p species are removed. The model also allows for cutting off the BD_p distribution at the high end. This effect was considered to be less likely in practice and was not investigated except that values were chosen above the point where further increases in the maximum allowable BD_p showed no effect on the calculated parameters.

IV. Summary

By their very nature, polyurethane block copolymers possess a certain degree of natural compositional heterogeneity. In an attempt to gain a more quantitative understanding of this effect, Monte Carlo simulations of polyurethane syntheses under various ideal reaction conditions were carried out. All of the simulations were deemed ideal from the standpoint that they used the same assumptions made by Peebles[1,18] in his theoretical study of polyurethane hard-segment-size distributions. The effects of varying the model parameters on the molecular weight and composition distributions were then systematically studied.

Probably the most important parameter influencing the molecular weight and composition distributions was the average block degree of polymerization ($\overline{BD}_p$), which is defined as the number of hard segments plus the number of soft segments in a chain. As $\overline{BD}_p$ decreased, the breadth of molecular weight distribution decreased while the compositional heterogeneity increased. The effect of $\overline{BD}_p$ can dominate or strongly influence the effects of some of the other parameters investigated such as the average hard-segment length, the soft-segment-size distribution, and the isocyanate reactivity ratio.

The effect of increasing the diisocyanate reactivity ratio (μ) was to make the hard-segment-size distribution more narrow. This in turn led to a slightly narrower molecular weight distribution and substantially less compositional heterogeneity. Increasing the average hard-segment length broadened the distribution of hard-segment sequence lengths, thereby increasing both the compositional heterogeneity and the breadth of the molecular weight distribution. These trends generally held true at a constant block degree of polymerization and for a constant conversion of monomers. As $\overline{\mathrm{BD}}_\mathrm{p}$ increased, the effects of varying the average hard-segment length and μ were diminished.

The effect of broadening the soft-segment molecular weight distribution was similar to that of decreasing μ or increasing the average hard-segment length. As the breadth of the soft-segment molecular weight distribution increased, the compositional heterogeneity increased and the molecular weight distribution became broader. Increasing the average hard- and soft-segment block lengths only influenced the compositional heterogeneity and molecular weight distribution if the distribution of segment lengths became broader as the average length increased.

Utilizing different hard-segment monomer species caused a change in the average hard-segment length necessary to achieve a given hard-segment weight fraction. Thus, using lower molecular weight diisocyanate and chain extender pairs produced a broader distribution of hard-segment lengths for a fixed hard-segment content than did the use of higher molecular weight diisocyanates and chain extenders. This resulted in polymers that had broader molecular weight distributions and were more compositionally heterogeneous.

Limiting the degree of polymerization to species longer than a chosen length is one way of modeling the process of precipitation in a solution polymerization, where the shorter chains emulsify in the solvent–nonsolvent system and are lost. The effect of eliminating the shorter chains was to increase the average molecular weight and degree of polymerization as well as to cause the molecular weight distribution to become narrower. The compositional heterogeneity also decreased. Eliminating the short chains has a much greater effect on the molecular weight and molecular weight distribution than did variations of any of the other parameters.

Acknowledgment. We acknowledge partial support of this research by the National Science Foundation, Division of Materials Science, Polymer Section, Grant No. DMR 81-06888, and through a grant from the Office of Naval Research.

Registry No. (MDI)·(BD)·(PTMO) (copolymer), 9018-04-6; (PTMO)·(TDI)·(ED) (copolymer), 73016-16-7.

References and Notes

(1) Peebles, L. H. *Macromolecules* **1974**, *7*, 872.
(2) Cooper, S. L.; Tobolsky, A. V. *J. Appl. Polym. Sci.* **1966**, *10*, 1837.
(3) Estes, G. M.; Cooper, S. L.; Tobolsky, A. V. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *4*, 313.
(4) Ferstandig, L. C.; Scherrer, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 4838.
(5) Brock, F. H. *J. Org. Chem.* **1959**, *24*, 1802.
(6) Miller, J. A.; Lin, S. B.; Hwang, K. K. S.; Wu, K. S.; Gibson, P. E.; Cooper, S. L. *Macromolecules* **1985**, *18*, 32.
(7) Wright, P.; Cummings, A. P. C. *Solid Polyurethane Elastomers*; McLaren and Sons: London, 1969.
(8) Harrell, L. L., Jr. *Macromolecules* **1969**, *2*, 607.
(9) Ng, H. N., Allegrezza, A. E.; Seymour, R. W.; Cooper, S. L. *Polymer* **1973**, *14*, 255.
(10) Pechhold, E.; Pruckmayr, G. *Rubber Chem. Technol.* **1980**, *53*, 1032.
(11) Vallance, M. A.; Castles, J. L.; Cooper, S. L. *Polymer* **1984**, *25*, 1734.
(12) Ceressa, R. J. *J. Polym. Sci., Part C* **1969**, *26*, 201.
(13) Harwood, H. J. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 394, 1051.
(14) Frensdorff, H. K. *Macromolecules* **1971**, *4*, 369.
(15) Helfand, E. *Macromolecules* **1972**, *5*, 301.
(16) Sorta, E.; Melis, A. *Polymer* **1978**, *19*, 1153.
(17) Lopez-Serrano, F.; Castro, J. M.; Macosko, C. W.; Tirrell, M. *Polymer* **1980**, *21*, 263.
(18) Peebles, L. H. *Macromolecules* **1976**, *9*, 58.
(19) Abouzahr, S.; Wilkes, G. L. *J. Appl. Polym. Sci.* **1984**, *29*, 2695.
(20) Skeist, I. *J. Am. Chem. Soc.* **1946**, *68*, 1781.
(21) Nielsen, L. E. *J. Am. Chem. Soc.* **1953**, *75*, 1435.
(22) Xu, M.; MacKnight, W. J.; Chen, C. H. Y.; Thomas, E. L. *Polymer* **1983**, *24*, 1327.
(23) Chen, C. H. Y.; Briber, R. M.; Thomas, E. L.; Xu, M.; MacKnight, W. J. *Polymer* **1983**, *24*, 1333.
(24) Bengston, B.; Feger, C.; MacKnight, W. J. *Polymer* **1985**, *26*, 895.
(25) Speckhard, T. A.; Ver Strate, G.; Gibson, P. E.; Cooper, S. L. *Polym. Eng. Sci.* **1983**, *23*, 336.
(26) Castro, J. M.; Lopez-Serrano, F.; Camargo, R. E.; Macosko, C. W.; Tirrell, M. *J. Appl. Polym. Sci.* **1981**, *26*, 2067.
(27) Castro, J. M.; Macosko, C. W.; Perry, S. J. *Polym. Commun.* **1984**, *25*, 83.
(28) Chang, A. L.; Briber, R. M.; Thomas, E. L.; Zdrahala, R. J.; Critchfield, F. E. *Polymer*, **1982**, *23*, 1061.
(29) Miller, J. A.; Speckhard, T. A.; Cooper, S. L. *Macromolecules*, following paper in this issue.
(30) Miller, J. A.; Speckhard, T. A.; Homan, J. G.; Cooper, S. L. submitted to *Polymer*.
(31) Speckhard, T. A.; Homan, J. G.; Miller, J. A.; Cooper, S. L. submitted to *Polymer*.
(32) Miller, J. A.; Cooper, S. L. *Makromol. Chem.* **1984**, *185*, 2429.
(33) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, *B43*, 25.
(34) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(35) Lowry, G. G., Ed. *Markov Chains and Monte Carlo Calculations in Polymer Science*; Marcel Dekker: New York, 1969.
(36) Bruns, W.; Motoc, I.; O'Driscoll, K. F. "Monte Carlo Applications in Polymer Science", *Lecture Notes in Chemistry*; Springer-Verlag: Heidelberg, 1981.
(37) Chaumont, P.; Gnanou, Y.; Hild, G.; Rempp, P. *Makromol. Chem.* **1985**, *186*, 2321.