Monte Carlo Simulation Study of the Polymerization of Polyurethane Block Copolymers. 2. Modeling of Premature Phase Separation during Reaction Using the Two-Phase Ideal Reaction Model

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

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.

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ABSTRACT: Several recent investigations have shown that premature phase separation during polymerization can affect the morphology and properties of polyurethane block copolymers. In particular, it has been suggested that reactant incompatibility can cause premature phase separation leading to a bimodal hard-segment-length distribution and excess compositional heterogeneity. In this investigation a Monte Carlo simulation is developed to explore the potential effects of premature phase separation on the composition, molecular weight, and hard-segment-length distributions of polyurethane block copolymers. Phase separation is modeled by partitioning the reactants into two phases and allowing each phase a different average degree of polymerization. Thus the final product is essentially a blend of two materials with different hard-segment length, composition, and molecular weight distributions. The simulation of polymerization in each phase then follows the procedure described previously, which incorporates several assumptions used by Peebles. Partitioning the reactants unevenly leads to bimodal composition and hard-segment-length distributions and broadens the molecular weight distribution. Having a different average degree of polymerization in the two phases leads to a much broader overall molecular weight distribution and a slight increase in compositional heterogeneity.

I. Introduction

In the first paper of this series[1] the polymerization of polyurethane block copolymers was simulated by using an ideal reaction model based on the assumptions of Peebles.[2,3] This model is useful for predicting and modeling the effects of various reaction parameters on the overall polymer molecular weight and composition distributions. In particular, as will be shown in a subsequent paper,[4] this model can be used to determine when experimental molecular weight and composition values indicate the existence of nonideal reaction conditions.

It was noted in the previous paper[1] that several investigations have indicated that one nonideal effect occurring in polyurethane polymerizations is premature phase separation. Castro et al.[5,6] showed by using viscosity and turbidity measurements on a one-step polyether polyurethane polymerization that phase separation occurred when the average hard-segment-sequence length was about 1.3. Subsequent work by Hager et al.,[7] using differential scanning calorimetry, and Camargo,[8] using Fourier transform infrared spectroscopy, found similar evidence for premature phase separation during polymerization of the same polyurethane system. In this system phase separation probably occurs due to segregation of longer hard segments (4,4′-methylenebis(phenyl isocyanate)/butanediol (MDI/BD)) either because they become incompatible with the soft segments as their length increases or because of their propensity to crystallize.[9]

MacKnight and co-workers[10,11] have provided strong evidence for the occurrence of macroscopic phase separation during a two-step bulk polymerization of polybutadiene-based polyurethanes. MacKnight et al. observed that when butanediol was added in the second step of the reaction, it formed a separate phase immediately. This behavior was observed for both crystallizable and noncrystallizable hard segments, indicating that the cause of the phase separation was not crystallization but the incompatibility of the reactants. The final polymers produced by reactions of this type were shown to have a bimodal hard-segment-length distribution and a broad molecular weight distribution;[12,13] in effect they could be thought of as a blend of a hard-segment-rich and a soft segment-rich material. The authors suggested a scenario for the polymerization where the isocyanate diffused into butanediol droplets and reacted to produce regions of virtually pure hard-segment polymer. The isocyanate-capped soft segments could not readily diffuse into the butanediol droplets and thus reacted primarily at the boundary between the two phases or by diffusion of butanediol into the soft-segment-rich phase. MacKnight et al.[10,11] also studied a polyether-based system similar to the one discussed above prepared by a two-step polymerization. For this system macroscopic phase separation was not observed immediately after the addition of the chain extender but rather at a later point in the reaction in accordance with the work of the other investigators noted above.[5-9]

If phase separation does occur during the polymerization of a polyurethane, it is apparent that using the single-phase ideal reaction model described previously[1] to calculate the composition and molecular weight distributions of the product is inappropriate. In this paper, a modified ideal reaction model is developed and described that simulates phase separation during polymerization. This model is termed the two-phase ideal reaction model and describes a two-phase polymerization by using two single-phase ideal polymerizations with the partitioning of the reactants occurring prior to polymerization. In the fourth paper of this series,[4] this model will be used along with other models to simulate the experimental data of MacKnight and co-workers[10-13] on polybutadiene polyurethanes. In this paper, the two-phase ideal reaction model is described, and the effects of varying the model parameters on the simulated composition, molecular weight, and hard-segment-length distributions are investigated.

II. Model Description

The approach used to model premature phase separation uses basically the same procedure as the single-phase ideal reaction model.[1] However, prior to building up any of the chains, the monomer species are partitioned into two separate phases, one that is rich in the polyol species and one that is rich in the diisocyanate species. The fraction of polyol in the polyol-rich phase along with the fraction

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* Author to whom correspondence should be addressed.

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

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of diisocyanate in the hard-segment-rich phase can be selected. The model then divides the chain extender so that the reaction mixture in each phase is stoichiometric. Stoichiometric reaction conditions are used for simplicity. It is likely that nonstoichiometric conditions exist in a real polymerization and thereby limit the degree of polymerization in each phase. After the monomers are divided between the two phases, an average degree of polymerization is chosen for each phase, since there is no reason to believe that the degree of polymerization of each phase will be identical.[9,14] The building up of chains in the two phases is then done in the same manner as described for the single-phase ideal reaction model. Finally, before the simulation of fractionation or calculation of the various distributions, the products of the two phases are recombined.

The degree of polymerization is assumed to follow a most probable distribution in each of the two phases. The degree of polymerization for both phases is defined in terms of the number of hard and soft blocks or segments in the chain instead of in terms of monomers. As discussed in the first paper,[1] this quantity is referred to as the block degree of polymerization BD_p and the error that is introduced by this approximation is fairly small at moderate to high values of the degree of polymerization. Another error associated with the use of the ideal reaction model is that of approximating the hard-segment-length distribution in each phase by the 100% conversion distributions given by Peebles.[2,3] It should be noted that although the hard-segment-length distribution of each phase follows the most probable distribution, the combined distribution will in general not follow the most probable distribution.

The parameters for this model include all of the parameters of the single-phase ideal reaction,[1] which include the overall sample stoichiometry; the type of monomers for the diisocyanate, the chain extender, and the polyol; the molecular weight and molecular weight distribution of the polyol; and the reactivity ratio of the two isocyanate functionalities of the diisocyanate. Additional parameters for the two-phase ideal reaction model include the fraction of diisocyanate in the hard-segment-rich phase, the fraction of polyol in the soft-segment-rich phase, the degree of polymerization of each phase, and the upper and lower bounds on the degree of polymerization in each phase, which are the values at which BD_p distributions are truncated. The reference case for this model is a 3/2/1 polymer of MDI, butanediol, and PTMO. The PTMO has a number-average molecular weight of 1008 and a weight-average molecular weight of 1450. The PTMO molecular weight distribution is that given by Miller et al.[15] The reactivity ratio of the diisocyanate (μ) is unity, and the average degree of polymerization of each phase is 30. The upper and lower bounds on the degree of polymerization are 1500 and 1, respectively. The fraction of MDI in the hard-segment-rich phase is 0.5, and the fraction of PTMO in the polyol-rich phase is also 0.5. The total number of chains used for the simulation is 15 000. This base case is identical with the reference case for the simulation in the first paper in this series except that the reactivity ratio of the diisocyanate is one rather than three. This is because a one-step polymerization, which we are primarily attempting to model here, is equivalent to a two-step reaction where the reactivity ratio of the diisocyanate is unity.[2,3]

The second part of the modeling procedure for the two-phase ideal reaction model involves a simulation of a solvent fractionation of the simulated sample, and the procedure used is identical with that described previously.[1] Although as noted in the first paper[1] 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 model starts with the chains with the lowest hard-segment content and sums their weight fraction until a value of 0.3 is reached. The average composition, number-average molecular weight ($\bar{M}_n$), and weight-average molecular weight ($\bar{M}_w$) of this fraction are then calculated. Similar quantities are also calculated for the remaining hard-segment-rich fraction.

This model is primarily designed for studying the premature phase separation phenomenon in a one-step bulk polymerization where phase separation occurs at the beginning of the reaction due to reactant incompatibility. This behavior is most likely to occur in bulk-polymerized systems with a large polarity difference between the soft-segment polyol and the chain extender, for example, polyisobutylene- or polybutadiene-based materials incorporating butanediol or ethylenediamine as a chain extender. The phenomenon may also occur when a solvent is used if the solvent is very poor (i.e., a nonsolvent) for one of the reactants. The model can also represent a two-step solution or bulk-state polymerization where phase separation occurs at the beginning of the second step since it does allow for a different reactivity for each of the isocyanate functionalities on the diisocyanate. However, in this case the model would be more accurate if partitioning occurred after the first step of the reaction was simulated. Also, to more accurately describe the behavior noted by MacKnight et al.,[10,11] the model would need to simulate the diffusion of species between the two phases, which causes the composition of the phases to change with time. Obviously, more complex modeling procedures are needed to simulate these effects. Similarly, modeling of systems where phase separation occurs after the average hard-segment length reaches a certain value will also require a more complex procedure; Tirrell et al.[9] have developed a model describing this situation. Obviously, the model used here presents a simplified picture of the polymerization process. However, its primary purpose is to qualitatively describe the effects of phase separation during or prior to polymerization on the molecular weight, hard-segment-length, and composition distributions. Therefore, even if the quantitative effects calculated by using this model rarely occur in an actual polymerization, it is hoped that the simulated trends will be correct. It may be possible by combining some of the concepts of this model with the simple sinking-pool model described in the third paper of this series[16] to more accurately simulate the complex situations described above. Finally, it should be noted that although it was developed independently, this model employs some similar concepts to the model developed by Tirrell et al.[9] noted above and a model for a bulk two-phase, free-radical polymerization developed by Ludwico and Rosen.[14]

The major errors involved in the use of the computer to implement the two-phase ideal reaction model involve the normal small errors associated with using a finite number of chains and round-off errors. Additional small errors are caused by approximating the hard- and soft-segment-length distributions and the degree of polymerization distribution by finite arrays. 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

Table I
Effect of Varying the Fraction of MDI in the Hard-Segment-Rich Phase and the Fraction of PTMO in the Soft-Segment-Rich Phase on the Chain Molecular Weight Distribution, the Hard-Segment-Length Distribution, and the Compositional Heterogeneity[a]

fraction of			hard segment	fractnl composition		phase composition	
MDI	PTMO	$\bar{M}_w/\bar{M}_n$	$\bar{K}_w/\bar{K}_n$	0.1	0.5	1	2
0.5	0.5	1.95	1.67	0.350	0.428	0.479	0.480
0.5	0.6	1.98	1.75	0.328	0.409	0.539	0.431
0.5	0.7	2.06	2.05	0.294	0.368	0.613	0.388
0.5	0.8	2.27	2.79	0.261	0.329	0.708	0.352
0.5	0.9	2.98	5.22	0.235	0.296	0.832	0.321
0.5	0.5	1.95	1.67	0.350	0.428	0.479	0.480
0.6	0.5	1.98	1.75	0.326	0.409	0.528	0.420
0.7	0.5	2.04	1.99	0.270	0.367	0.569	0.342
0.8	0.5	2.15	2.39	0.197	0.328	0.603	0.241
0.5	0.5	1.95	1.67	0.350	0.428	0.479	0.480
0.6	0.6	2.04	2.00	0.285	0.365	0.586	0.370
0.7	0.7	2.36	3.19	0.200	0.260	0.692	0.256
0.75	0.75	2.66	4.31	0.163	0.208	0.743	0.199

[a] 3/2/1 MDI/BD/PTMO-1000(H); $BD_p = 30$ in each phase.

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

The reference parameters described in the previous section produce a simulated material with the following molecular weight and composition distributions. The number-average molecular weight is 28 400, and the value of $\bar{M}_w/\bar{M}_n$ is 1.95. The hard segment $\bar{K}_w/\bar{K}_n$, which is the polydispersity index of the hard-segment-length distribution, is 1.66. $\bar{K}_w$ and $\bar{K}_n$ are the weight- and number-average hard-segment lengths measured in terms of the number of diisocyanate monomers contained in a hard segment.[17] In an ideal one-phase polymerization $\bar{K}_w$ and $\bar{K}_n$ are only affected by the stoichiometry, the conversion, and the isocyanate reactivity ratio. These effects have been described by Peebles[2,3] and thus were not included in the discussion of the single-phase ideal reaction model,[1] which in any event does not include the effect of conversion since the distribution at 100% conversion is always used. In the two-phase model presented here $\bar{K}_w$ and $\bar{K}_n$ exhibit the expected behavior in each of the two phases. However, when the overall values are calculated, because of the nature of the weighting process, $\bar{K}_w$ and thus $\bar{K}_w/\bar{K}_n$ can acquire values different from the expected value based on the overall stoichiometry and conversion ($\bar{K}_n$ will have the expected value). The fractional compositions of the 10% and 50% soft-segment-rich fractions are 35.0 and 42.8 wt % hard segment, respectively, while the overall composition is 48.1 wt % hard segment. The conversion for this case is 98.9%. These values are in agreement with the values determined by using the single-phase ideal reaction model with $\mu = 1$ (see Table II in ref 1) as expected. Also, the effects of varying parameters such as the diisocyanate reactivity ratio (μ) and the average degree of polymerization on the molecular weight and composition distributions are the same as were noted for the single-phase ideal reaction model[1] as long as the monomers are partitioned evenly and the degree of polymerization is the same in both phases. Even when the monomers are not partitioned evenly or the degree of polymerization is not the same in each phase, the effects of varying μ, the average hard-segment content, the soft-segment molecular weight and molecular weight distribution, the soft- or hard-segment type, and the minimum BD_p values follow the same trends noted for the single-phase ideal reaction model.[1] Furthermore, the effects of these variables are generally small compared to the effects of the variables used to simulate phase separation. Thus, in this section only the effects of varying the monomer partitioning and the $\overline{BD}_p$ of each phase of the hypothetical samples will be investigated.

Table I shows the effects of changing the fraction of the total diisocyanate that is present in the hard-segment-rich phase (phase 1) and the fraction of polyol in the soft-segment-rich phase (phase 2). The other parameters of the model are held constant at their base values. The first set of entries in Table I indicates that increasing the amount of polyol species in phase 2 while keeping the amount of MDI species in each phase constant leads to broader molecular weight and hard-segment-length distributions and a larger difference in the composition of the two phases. Also, the fractional compositions at 0.1 and 0.5 soft-segment-rich weight fraction show a greater deviation from the average composition (48.1% for all of the cases shown in Table I), indicating an increase in the compositional heterogeneity.[1] These effects can be explained in the following manner. Increasing the amount of polyol in phase 2 while holding the amount of MDI constant leads to a lower average hard-segment content and shorter hard segments in phase 2, giving rise to a broader hard-segment-length distribution. Since phase 2 has on average shorter hard segments, the molecular weight of a molecule in phase 2 with the same BD_p as a molecule in phase 1 will have a lower molecular weight, resulting in a broader molecular weight distribution for the final material. The lower average hard-segment content of phase 2 also gives rise, as expected, to a broader composition distribution.[10]

Figure 1 illustrates the increase in the compositional heterogeneity when the fraction of polyol species in the soft-segment-rich phase is increased. The x axis in Figure 1 is the cumulative weight fraction of chains in ascending order of hard-segment composition. As x 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 termed the specific hard-segment weight fraction. A completely homogeneous material would exhibit a horizontal line at the average composition. When the polyol species are evenly divided (0.5), the composition curve is the same as observed for the single-phase ideal reaction model.[1] As the fraction of polyol in the soft-segment-rich phase increases,

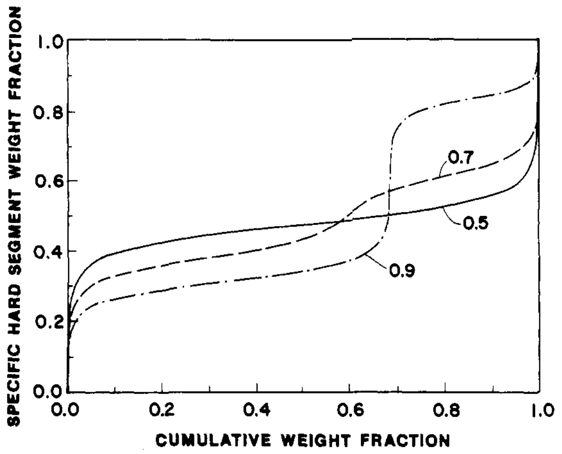

Figure 1. Specific hard-segment weight fraction vs. cumulative weight fraction for the reference case with each phase containing half of the diisocyanate and one phase containing 50%, 70%, and 90% of the polyol.

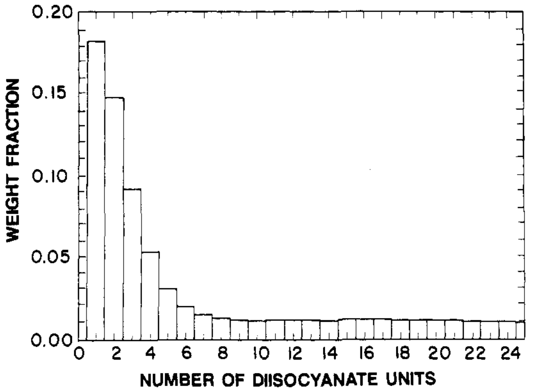

Figure 2. Hard-segment-length distribution (weight fraction) for the reference case with 90% of the polyol in phase 2 and the diisocyanate divided evenly.

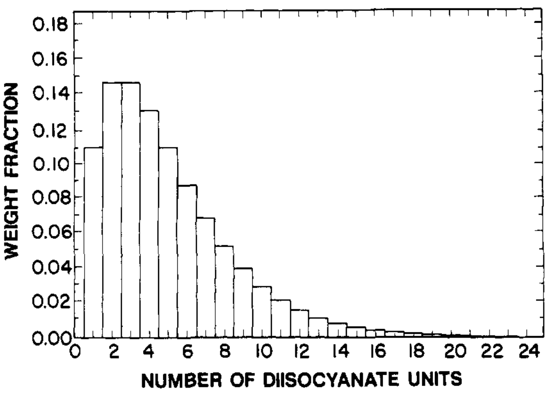

Figure 3. Hard-segment-length distribution (weight fraction) for the reference case (most probable distribution).

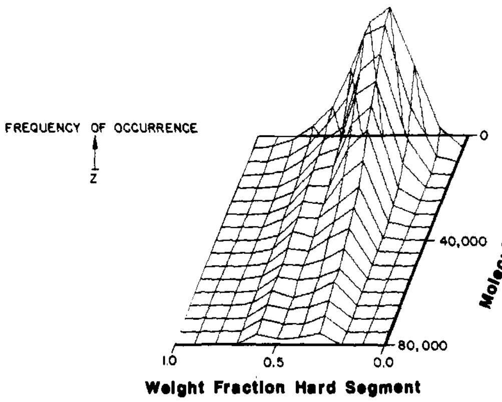

Figure 4. Three-dimensional histogram of the molecular weight, the weight fraction of hard segment, and the relative frequency of occurrence for the reference case with each phase containing half of the diisocyanate and one phase containing 70% of the polyol.

the composition distribution exhibits two plateaus, with one plateau at about the average hard-segment content of each of the two phases. The breadth of each plateau is roughly proportional to the weight fraction of that phase. Thus, the data in Figure 1 for the hypothetical material with 90% of the polyol in phase 2 can be thought of as a 65:35 blend by weight of a material of about 30% hard-segment content and a material of about 85% hard-segment content.

The effect of dividing the polyol unevenly between the phases on the hard-segment-sequence-length distribution can be seen in Figure 2. Figure 2 is a histogram of the number fraction of hard segments weighted by their length (in terms of number of diisocyanate units) vs. hard-segment length. The distribution displayed in Figure 2 is for a hypothetical sample with 90% of the polyol in phase 2 and the MDI evenly divided. For this sample the molar stoichiometry in phase 1 is 15/14/1 (MDI/BD/PTMO), while in phase 2 the stoichiometry is approximately 1.67/0.67/1.0. The distribution drops sharply between 1 and 4 MDI units, reflecting primarily the distribution of short hard segments in the polyol-rich phase. The small shoulder or peak at a hard-segment length of about 15 reflects the average hard-segment length of the hard segments in the isocyanate-rich phase. For comparison, Figure 3 displays the hard-segment distribution for the case where both the polyol and isocyanate are evenly divided, and thus the hard-segment lengths follow a most probable distribution.

Figure 4 also shows the effect of dividing the polyol unevenly between the two phases (70% in phase 2). This figure is a three-dimensional histogram as previously discussed[1] where the x–y plane is a grid of composition and molecular weight values and the z axis represents the number of chains whose composition and molecular weight lie in each particular sector. The data in Figure 4 exhibit two ridges indicative of two well-defined phases, each of which has a fairly narrow composition range. These ridges lie at approximately the average hard-segment content of each of the two phases and correspond to the plateaus in Figure 1. As noted previously,[1] the composition distribution does become narrower as the molecular weight or degree of polymerization increases, and this effect can also be observed in Figure 4. The data in Figures 1–4 and Table I clearly show the large effects on the composition, molecular weight, and hard-segment-length distributions of dividing the polyol unevenly between the two phases. In particular, relatively large values of $\bar{K}_w/\bar{K}_n$ can be produced.

A similar situation exists when the fraction of diisocyanate in the hard-segment-rich phase (phase 1) is increased while the fraction of the polyol in each phase is held constant. The second set of entries in Table I shows that the molecular weight, composition, and hard-segment-length distributions become broader as the fraction of MDI in phase 1 increases. The effect on the compositional heterogeneity is illustrated by Figure 5, which again shows the development of two plateaus at about the average hard-segment contents of the two phases as the fraction of diisocyanate in phase 1 is increased. A careful examination of Table I reveals that dividing the diisocyanate unevenly has slightly less effect on the molecular weight and hard-segment-length distributions than divid-

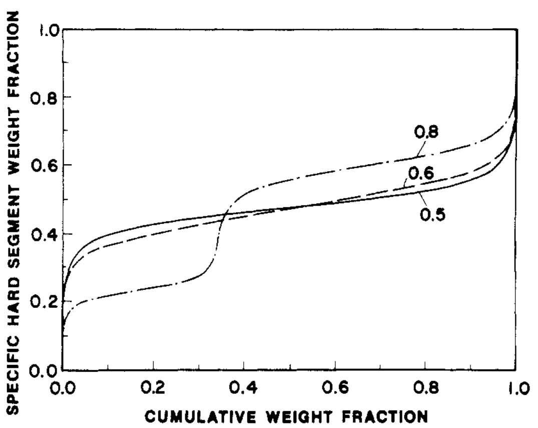

Figure 5. Specific hard-segment weight fraction vs. cumulative weight fraction for the reference case with each phase containing half of the polyol and one phase containing 50%, 60%, and 80% of the diisocyanate.

ing the polyol unevenly. For example, with 80% of the polyol in phase 2 and the diisocyanate divided evenly, $\bar{M}_w/\bar{M}_n$ is equal to 2.98, while in the reverse case (80% of diisocyanate in phase 1 and the polyol divided evenly), $\bar{M}_w/\bar{M}_n$ is 2.15. Similar trends are observed for $\bar{K}_w/\bar{K}_n$. Since in both cases $\bar{K}_n$ and $\bar{M}_n$ are the same, the difference between the two cases must be in the values of $\bar{K}_w$ and $\bar{M}_w$. This behavior can be understood if the stoichiometry of the phases is calculated. For the first case described above the phase 1 stoichiometry is 7.5/6.5/1.0, while the phase 2 stoichiometry is 1.875/0.875/1.0. In the second case (diisocyanate divided unevenly) the stoichiometries of phase 1 and phase 2 are 4.8/3.8/1.0 and 1.2/0.2/1.0, respectively. Thus, in the first case there will tend to be a few more longer hard segments, which, because of the weight averaging, will produce a higher value of $\bar{K}_w$ and thus $\bar{M}_w$. The differences in stoichiometries between the two cases are a natural result of there being more diisocyanate monomers than polyol monomers in an overall 3/2/1 material and the fact that stoichiometric ratios of isocyanate and hydroxyl groups in each phase must be maintained. It should be noted that these effects also place different restrictions on the division of the monomers. For example, if the polyol is divided evenly in a 3/2/1 material, the highest allowable fraction of diisocyanate in phase 1 is 0.833. For the reverse case there is no restriction on the division of the polyol.

It should also be noted that from the data in Table I it would appear that in the case of the compositional heterogeneity, as measured by the deviation of the fractional compositions from the average composition, the effect of dividing the diisocyanate unevenly is greater than the effect of dividing the polyol unevenly. This result is due to the fact that the fractional compositions are very sensitive to small amounts of very high soft-segment-content material. (Note that if the summation started with high hard-segment-content material, the fractional compositions would be sensitive to small amounts of material with a very high hard-segment content.) From the stoichiometries listed above it is clear that when the diisocyanate is divided unevenly (at the same fraction of diisocyanate in phase 1 as the comparable sample with a greater fraction of polyol in phase 2), the hard-segment content of phase 2 will be lower, giving rise to lower fractional compositions. This effect is most pronounced at fractional compositions of 0.1 and is almost negligible at fractional compositions of 0.5.

The last set of entries in Table I shows data where both the polyol and the diisocyanate are divided unevenly. As one might expect, the same trends are observed as when either the polyol or the diisocyanate is divided unevenly. The magnitude of the effects cannot be easily compared to the cases where only one of the species is divided unevenly. To a first approximation the case where both the polyol and diisocyanate are divided 60/40 is equivalent to the average of the two cases where one species is divided 70/30 and the other species is divided evenly.

Table II
Effect of Varying the Degree of Polymerization in Each Phase on the Chain Molecular Weight Distribution, the Hard-Segment-Length Distribution, and the Compositional Heterogeneity[a]

$\overline{\mathrm{BD}}_p$ in phase				fractnl composition	
1	2	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	0.1	0.5
10	10	18100	1.93	0.247	0.387
10	20	27400	2.18	0.279	0.401
10	30	37100	2.62	0.290	0.407
10	40	47000	3.09	0.295	0.410
10	50	54900	3.49	0.298	0.413
10	60	66500	4.06	0.302	0.416
20	20	37100	1.95	0.321	0.417
20	40	54900	2.17	0.341	0.426
20	60	75100	2.61	0.351	0.430
30	30	55400	1.95	0.350	0.428
30	40	64200	1.98	0.357	0.430
30	50	74500	2.07	0.364	0.433
30	60	82600	2.17	0.369	0.436
40	40	73500	1.92	0.366	0.435
40	50	84000	1.97	0.375	0.437
40	60	92300	2.00	0.378	0.439
50	50	91700	1.92	0.380	0.440
50	60	101000	1.93	0.385	0.441
60	60	111000	1.92	0.390	0.444

[a] 3/2/1 MDI/BD/PTMO-1000(H). Each phase has same composition.

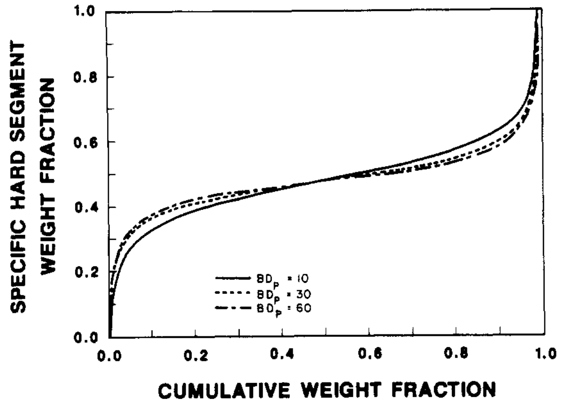

Figure 6. Specific hard-segment weight fraction vs. cumulative weight fraction for the reference case with $\overline{\mathrm{BD}}_p$ in one phase equal to 10 and the BD_p of the other phase equal to 10, 30, and 60.

Table II lists the results of the simulation for the two-phase ideal reaction model for the reference parameters (note that the monomers are evenly divided) where the average block degree of polymerization ($\overline{\mathrm{BD}}_p$) in each phase is changed. Within each group, as the $\overline{\mathrm{BD}}_p$ of one of the phases increases and the difference between the $\overline{\mathrm{BD}}_p$'s of the two phases increases, the breadth of the molecular weight distribution increases as expected.[9] The compositional heterogeneity decreases with increasing $\overline{\mathrm{BD}}_p$ of either phase due to the increase in the average BD_p of the system. This is illustrated by Figure 6, which shows

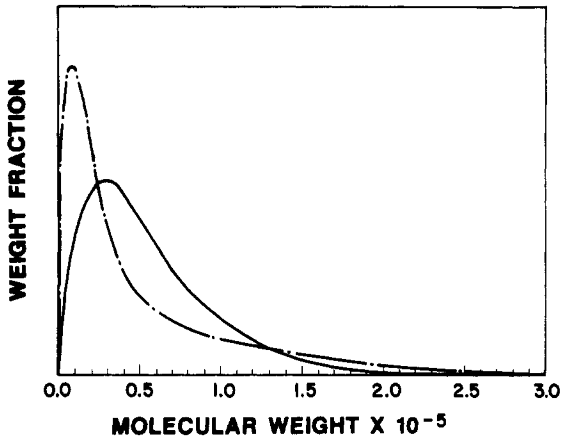

Figure 7. Molecular weight distributions for the reference case with block degrees of polymerization of the two phases of 10,50 (·–) and 30,30 (—), respectively.

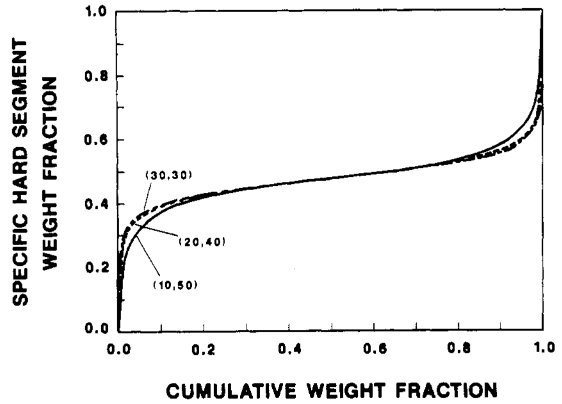

Figure 8. Specific hard-segment weight fraction vs. cumulative weight fraction for the reference case with values for $\overline{\mathrm{BD}}_\mathrm{p}$ in the two phases of 30,30, 20,40, and 10,50, respectively.

specific hard-segment content vs. cumulative weight fraction data for the reference case with a $\overline{\mathrm{BD}}_\mathrm{p}$ of 10 in one phase and $\overline{\mathrm{BD}}_\mathrm{p}$'s of 10, 30, and 60 in the second phase. At a constant weight-average molecular weight (the runs of 10,50 and 20,40 and 30,30 are examples), the molecular weight distribution is broadened as the difference between the $\overline{\mathrm{BD}}_\mathrm{p}$ of each phase increases. Figure 7 shows the molecular weight distribution (on a weight fraction basis) for the 30,30 (most probable distribution) and the 10,50 runs of Table II. As expected, the 10,50 case has a greater number of both very low and very high molecular weight chains. The compositional heterogeneity is also greater for the cases where the difference in the $\overline{\mathrm{BD}}_\mathrm{p}$ between the phases is the largest, but the effect as shown in Figure 8 is small compared to the effect of dividing the monomers unevenly. It should be noted that there are no $\bar{K}_\mathrm{w}/\bar{K}_\mathrm{n}$ values listed in Table II because the average hard-segment length and the hard-segment-length distribution depend only on μ and the stoichiometry of the phases. This behavior is a consequence of using the hard-segment distribution for 100% conversion in the modeling regardless of the conversion for a particular model simulation. Peebles[2] showed that as the conversion (or degree of polymerization in terms of monomers) increased, the number-average hard-segment length also increased. Thus one would expect that the hard-segment distribution would be slightly broader for the 20,40 case than for the 30,30 case.

Table III shows the effect of varying the block degree of polymerization in the two phases when the polyol is unevenly distributed between the two phases. Two different types of behavior are observed, depending upon which phase is held at a fixed $\overline{\mathrm{BD}}_\mathrm{p}$. When the hard-segment-rich phase (phase 1) is fixed at a $\overline{\mathrm{BD}}_\mathrm{p}$ of 30 while the $\overline{\mathrm{BD}}_\mathrm{p}$ of the soft-segment-rich phase (phase 2) is increased (first set of entries in Table III), a decrease in the breadth of the molecular weight distribution is seen along with a decrease in the compositional heterogeneity of the system. The diisocyanate and the polyol are distributed for this simulation such that the stoichiometry of the first phase is 7.5/6.5/1.0, while that of the second phase is 1.875/0.875/1.0. Thus, the average block molecular weight in the first phase is 1740, while in the second phase the average is 780. Thus, increasing the $\overline{\mathrm{BD}}_\mathrm{p}$ of the second phase will cause the two phases to have molecular weights and distributions that are more similar as the ratio of the $\overline{\mathrm{BD}}_\mathrm{p}$'s of the two phases approaches 1740/780, or about 2.2. The case where the first phase has a $\overline{\mathrm{BD}}_\mathrm{p}$ of 30 and the second phase has a $\overline{\mathrm{BD}}_\mathrm{p}$ of 50 comes closest to this condition and has the lowest overall $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$. The compositional heterogeneity also decreases as the phase 2 $\overline{\mathrm{BD}}_\mathrm{p}$ increases. This can be attributed to the increase in the average BD_p of the polyol-rich phase. As discussed above, the fractional compositions are most sensitive to the composition distribution of the soft-segment-rich material which becomes narrower as the phase 2 $\overline{\mathrm{BD}}_\mathrm{p}$ increases.

Table III
Effect of Varying the Degree of Polymerization in Each Phase on the Chain Molecular Weight Distribution, the Hard-Segment-Length Distribution, and the Compositional Heterogeneity for a Case where the Composition of the Phases is Different[a]

$\overline{\mathrm{BD}}_\mathrm{p}$ in phase				fractnl composition	
1	2	$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$	0.1	0.5
30	10	10900	4.27	0.195	0.312
30	20	20400	2.73	0.240	0.323
30	30	28400	2.27	0.261	0.329
30	40	35600	2.06	0.274	0.333
30	50	42000	1.98	0.283	0.335
10	30	20300	1.99	0.258	0.326
20	30	25900	2.05	0.261	0.329
30	30	28400	2.27	0.261	0.329
40	30	30100	2.54	0.262	0.330
50	30	30900	2.77	0.260	0.329
10	10	9370	2.26	0.191	0.308
20	10	10500	3.27	0.195	0.312
30	10	10800	4.27	0.195	0.312
40	10	11100	5.34	0.196	0.312

[a] 3/2/1 MDI/BD/PTMO-1000(H). Diisocyanate divided 50/50; polyol divided 20/80.

The effects of changes in the phase 1 BD_p at a constant phase 2 $\overline{\mathrm{BD}}_\mathrm{p}$ (second set of entries in Table III) are different than the reverse case discussed above, but can be explained in a similar manner. As the phase 1 $\overline{\mathrm{BD}}_\mathrm{p}$ increases, the difference in the average molecular weights of the two phases increases (note that for the 10,30 case the number-average molecular weight of phase 2 is slightly higher than the $\bar{M}_\mathrm{n}$ for phase 1; in all the rest of the cases $\bar{M}_\mathrm{n}$ of phase 1 is higher), which leads to the observed increase in the breadth of the molecular weight distribution. The fractional composition data are more complex. In general, one might expect the compositional heterogeneity to decrease due to the increase in the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 1. However, the data in Table III indicate almost no effect of varying the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 1 on the fractional composi-

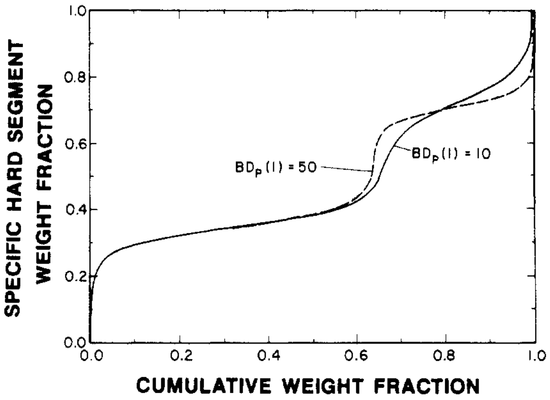

Figure 9. Specific hard-segment weight fraction vs. cumulative weight fraction for the reference case with 80% of the polyol in phase 2, the diisocyanate divided evenly, $\overline{\mathrm{BD}}_\mathrm{p}$ (2) = 30, and $\overline{\mathrm{BD}}_\mathrm{p}$ (1) = 10 and 50.

tions. This is because the fractional composition data are most sensitive to composition changes in the polyol-rich phase. Figure 9 shows the composition distributions for the 10,30 and 50,30 cases of Table III. Note that increasing the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 1 flattens the plateau at the average hard-segment content of phase 1 but has a negligible effect on the composition data below a weight fraction of 0.6. In general, the cumulative fractional composition data presented in Tables I–III do not always produce meaningful comparisons when the differences in the distributions are primarily in the high hard-segment-content range.

The final set of entries in Table III also shows the effects of varying the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 1 while the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 2 is held constant; in this case the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 2 is 10. The same trends with the BD_p of phase 1 are observed, but the effect on $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ is larger. These data are displayed to indicate the large values of $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ that can be obtained by using this model. (Values of $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ up to about 15 can be obtained when the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 1 is much larger than the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 2. However, in those cases either the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 1 is so high that the errors caused by the use of the finite BD_p array are no longer negligible or the $\overline{\mathrm{BD}}_\mathrm{p}$ of phase 2 is so low that the errors resulting from defining the degree of polymerization in terms of segments instead of monomers and the use of the hard-segment distribution at 100% conversion become noticeable). It should also be noted that Table III does not contain values for $\bar{K}_\mathrm{w}/\bar{K}_\mathrm{n}$ of the hard segments. As discussed in regard to Table II, this is because in this model the hard-segment-length distribution is not influenced by the degree of polymerization. Thus, all the entries in Table III have the same hard-segment distribution ($\bar{K}_\mathrm{n} \doteq 3$, $\bar{K}_\mathrm{w}/\bar{K}_\mathrm{n} = 2.78$).

IV. Summary

The effects of premature phase separation on the composition, molecular weight, and hard-segment-length distributions of polyurethane block copolymers have been investigated by using a Monte Carlo simulation method. Phase separation was modeled by partitioning the monomers into two phases prior to reaction and allowing for a different average degree of polymerization in each phase. Polymerization in each phase is then simulated following the same procedure described previously,[1] which incorporates assumptions of ideal behavior proposed by Peebles.[2] The model parameters include all of the parameters of the single-phase ideal reaction model[1] along with the fraction of isocyanate and polyol in each of the phases and the average block degree of polymerization of each phase.

Varying the parameters of the single-phase ideal reaction model produced similar effects on the molecular weight and composition distributions noted previously[1] and were not discussed. Increasing the fraction of the polyol in one of the phases while the isocyanate is evenly divided resulted in a broader molecular weight distribution and the development of broad bimodal hard-segment-length and composition distributions. Similar effects were observed when the isocyanate was divided unevenly while the polyol was divided evenly or when both species were divided unevenly.

Having a different average block degree of polymerization in the two phases when the monomers are divided evenly leads to a slight increase in compositional heterogeneity and a much broader molecular weight distribution ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$ can be 10 or greater). When both the composition and the average degree of polymerization in each phase are different, the above effects are combined and the materials are essentially a blend of two materials with different composition, molecular weight, and hard-segment-length distributions.

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Registry No. (MDI)·(BD)·(PTMO) (copolymer), 9018-04-6.

References and Notes

(1) Speckhard, T. A.; Miller, J. A.; Cooper, S. L. *Macromolecules*, preceding paper in this issue.
(2) Peebles, L. H. *Macromolecules* **1974**, *7*, 1872.
(3) Peebles, L. H. *Macromolecules* **1976**, *9*, 58.
(4) Speckhard, T. A.; Homan, J. G.; Miller, J. A.; Cooper, S. L., submitted to *Polymer*.
(5) Castro, J. M.; Lopez-Serrano, F.; Camargo, R. E.; Macosko, C. W.; Tirrell, M. *J. Appl. Polym. Sci.* **1981**, *26*, 2067.
(6) Castro, J. M.; Macosko, C. W.; Perry S. J. *Polym. Commun.* **1984**, *25*, 83.
(7) Hager, S. L.; MacKury, T. B.; Gerkin, R. M.; Critchfield, F. E. *Adv. Chem. Series* **1981**, *172*.
(8) Camargo, R. E. Ph.D. Thesis, University of Minnesota, 1983.
(9) Tirrell, M.; Lee, L. S.; Macosko, C. W. In *Polymerization Reactors and Processes*; Henderson, J. N., Bouton, T. C., Eds.; 1978; *ACS Symp. Ser. 104*, 149.
(10) Xu, M.; MacKnight, W. J.; Chen, C. H. Y.; Thomas, E. L. *Polymer* **1983**, *24*, 1327.
(11) Chen, C. H. Y.; Briber, R. M.; Thomas, E. L.; Xu, M.; MacKnight, W. J. *Polymer* **1983**, *24*, 1333.
(12) Bengston, B.; Feger, C.; MacKnight, W. J. submitted to *Polymer*.
(13) Chen-Tsai, C. H. Y. Ph.D. Thesis, University of Massachusetts, 1985.
(14) Ludwico, W. A.; Rosen, S. L. *J. Appl. Polym. Sci.* **1975**, *19*, 757.
(15) Miller, J. A.; Cooper, S. L. *Makromol. Chem.* **1984**, *185*, 2429.
(16) Miller, J. A.; Speckhard, T. A.; Homan, J. G.; Cooper, S. L. submitted to *Polymer*.
(17) Miller, J. A.; Lin, S. B.; Hwang, K. K. S.; Wu, K. S.; Gibson, P. E.; Cooper, S. L. *Macromolecules* **1985**, *18*, 32.