domains of different densities. This conflict does not in fact occur; these domains can exist as long as they do not interfere with the statistical properties of each molecular chain.

All the models of polymeric systems now proposed must take these facts into account.

Acknowledgments. This work was made possible by the CNRS who gave financial aid in the form of an ATP and by the allocation of beam time on the D 11 apparatus at the Institute Laue-Langevin (Grenoble, France). We are grateful to Dr. K. Ibel of this Institute for discussions about the use of the apparatus and to M. Rebesco and Mr. Barthelemy for assistance in running it. We would like to thank Dr. D. Cribier (CEA-SRM) for his constant help and fruitful discussions during the experiments. We also appreciate the help of Mr. M. Herbert (CEA Département des Radioéléments) in obtaining deuterated monomers.

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Sequence Length Distribution in Segmented Block Copolymers

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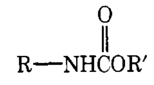
ABSTRACT: The effect of the nonequivalent reactivity of the two functional groups in a diisocyanate on the sequence length distribution in segmented block copolymers is calculated on a kinetic basis for a number of polymerization recipes. In the two-stage recipe, excess diisocyanate monomer first reacts completely with an intermediate molecular weight prepolymer then a low molecular weight extender is added. Alteration of the definition of the hard block segment in the two-stage process demonstrates that the distribution follows the most probable form. The heterogeneity index is less than 2 because of the relatively short sequence lengths. The number average length of the hard block segment under stoichiometric conditions at 100% conversion is equal to A_1/B_1 when the isocyanate groups are equally reactive, where A_1 is the initial concentration of diisocyanate and B_1 is the initial concentration of prepolymer. When the reactivity of the first isocyanate group becomes appreciably greater than that of the second isocyanate group, the number average length of the hard block segment approaches $(A_1 - B_1)/B_1$. The sequence length distribution of the hard blocks, the amount of internal sequences, and the molecular weight of the polymer can be varied by alteration of the polymerization recipes and the method of mixing the components.

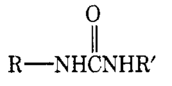
Segmented polyurethanes are usually prepared by reacting a diisocyanate (AA) with a hydroxy-terminated polyester or polyether (BB) to form a soft block segment. The initial content of diisocyanate (AA) exceeds that of the prepolymer (BB) so that there will always be an excess of unreacted diisocyanate. The resultant polymer is then extended with a low molecular weight diol or a low molecular weight diamine (CC) to form a hard block segment. During the fabrication of the final article, the hard block portions segregate from the soft block segments to form a microheterogeneous composite.[2]

The reactions involved in this process are rather complex. The urethane bonds I formed from the reaction of isocyanate with hydroxyl and the urea bonds II formed from the reaction of isocyanate with amine are somewhat reversible. If any water is present in the system, it will react with an isocyanate group to eventually form an amine plus CO_2 gas; the amine can then react further with an isocyanate group. Branching and cross-linking reactions can occur by reaction of an active hydrogen from a urethane or a urea group with an isocyanate group to form allophonate III or biuret IV groups, respectively. In the presence of catalysts, the isocyanate groups self-polymerize to uretidione V, isocyanurate VI, or a linear polymer VII of high molecular weight. Furthermore, it has been demonstrated that the reactivity of a given isocyanate group in a diisocyanate monomer may depend strongly on whether or not the other isocyanate group has reacted.[3a]

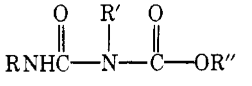
Because of these complex reactions, little attention has been paid to the kinetics of polymerization and, in particular, to the precise composition of the soft and hard block segments. The mechanical properties of segmented polyurethanes depend strongly on the micromorphology of the finished polymer which in turn depends upon the hard and soft block composition and on the processing details. A very precise study of the effects of segment length and distribution has been undertaken by Harrell,[3b] who combined monodisperse hard segments of various lengths with soft


$R{-}NH\overset{\overset{O}{\|}}{C}OR'$

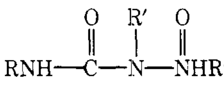
I


$R{-}NH\overset{\overset{O}{\|}}{C}NHR'$

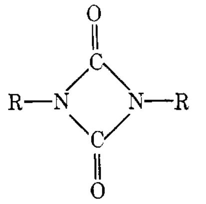
II


$RNH\overset{\overset{O}{\|}}{C}{-}\overset{\overset{R'}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}OR''$

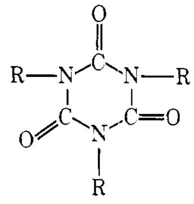
III


$RNH{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{R'}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}NHR''$

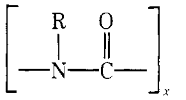
IV



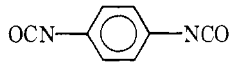
V



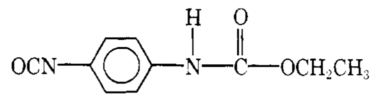
VI


$\left[{-}\overset{\overset{R}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}\right]_x$

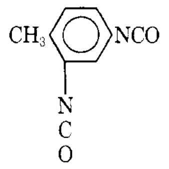
VII



VIII



IX



XII = TDI

segments under stoichiometric conditions. Harrell found that thermal and mechanical properties of the polymers did depend on the length and distribution of both the hard and soft segments. An alternative method is to vary the hard block composition by using different polymerization recipes. Several recent publications have been addressed to this problem, but the hard and soft segments are specified by the initial composition of the reactants and not by the statistical probability based on the reactivity of the functional groups involved.[4]

Let us consider for the moment the reaction of 2 equiv of AA with 1 equiv of BB and assume that all molecules are equally reactive independent of molecular weight. The statistics of the system require that when all of BB has reacted, all molecules are capped with A-type ends. The mole fraction of unreacted AA monomer is 0.5, the mole fraction of AABBAA is $(0.5)^2$, that of $AA(BBAA)_2$ is $(0.5)^3$, etc. It is easily seen that if an A-type end of a monomer reacts faster than an A-type end of a polymer molecule, then molecules of BB will tend to be capped by AA, leading to a decrease in the amount of high molecular weight polymer and in the amount of unreacted AA. On the other hand, if the A-type end of a monomer reacts slower than an A-type end of a polymer molecule, the distribution is shifted toward an increase in the amount of high molecular weight polymer and in the amount of unreacted AA. Thus, the composition of the hard block segment will depend on the relative reactivity of the isocyanate units, the initial concentration of the reactants, and the procedure used to mix the reacting components.

It is the purpose of this paper to calculate the number average molecular weight of the polymer before and after the addition of extender, the average length of the hard block segment in the extended polymer, and the distribution of the hard block segment length. The variables to be considered are the initial concentration of the reactants A_1, B_1, and C_1; the relative reactivity of the diisocyanate groups, μ; the conversion of the extension reaction; and the sequence of combining the components AA, BB, and CC.

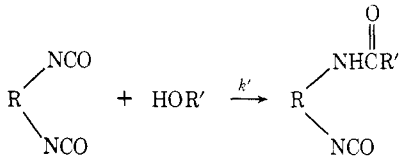
Table I
Relative Reactivities for the Consecutive Reactions of Diisocyanates with Two Representative Alcohols

	Relative rate constants			
	Ethanol[a]		1-Butanol[b]	
Diisocyanate	k_1	k_1/k_2	k_1	k_1/k_2
m-Phenylene			11	8.4
p-Phenylene			7.7	9.2
4,4′-Diphenylmethane	2.3	3.2	2.4	2.9
2,6-Tolylene			2.2	6.1
2,4-Tolylene	3.0	25	4.9	11.9
3,3′-Dimethyl-4,4′-diphenylmethane			0.41	2.4
Durene			0.05	2.6
1,5-Naphthalene	2.7	3.5		
1,3-Xylylene	0.20	2.5		
1,4-Xylylene	0.18	1.9		
5-*tert*-Butyl-1,3-xylylene	0.19	2.7		
1,6-Hexamethylene			0.001	2.0
Phenyl isocyanate (standard)	(1.0)		(1.0)	

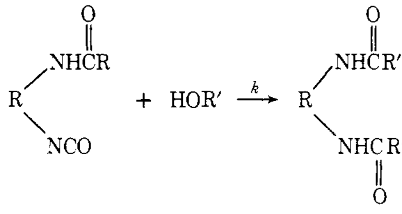
[a] In toluene at 30°, excess ethanol.[6] [b] In toluene at 40°, with triethylamine catalyst.[7]

General Treatment

Table I, taken from Lenz,[5] gives the ratio of the first reaction rate constant of an isocyanate group to the second reaction rate constant for a number of diisocyanates with two aliphatic alcohols. One can speculate that the electron donating or withdrawing character of a substituent on a benzene ring can materially influence the reactivity of a given isocyanate; for instance, *p*-phenylene diisocyanate VIII as compared to 4-(imino carbonyloxyethane)phenyl isocyanate IX. On the other hand, it is not easy to see how the reactivity of one end of hexamethylene isocyanate can be influenced by the structure at the other end by invoking electronegativity effects. A proximity effect is suggested by


$$R(NCO)_2 + HOR' \xrightarrow{k'} R(NH\overset{\overset{O}{\|}}{C}R')(NCO) \quad (1)$$

X XI


$$R(NH\overset{\overset{O}{\|}}{C}R)(NCO) + HOR' \xrightarrow{k} R(NH\overset{\overset{O}{\|}}{C}R')(NH\underset{\underset{O}{\|}}{C}R') \quad (2)$$

eq 1 and 2, where the proximity effect is rate controlling[5] but no spatial details are given.

Another way of expressing eq 1 and 2 is to state that the reactivity of the monomer X is different from that of the polymer XI. The relative reactivity of the diisocyanate groups is $\mu = k'/k$.

The above arguments can be applied to any symmetrical molecule such as those cited in Table I. This will be called the symmetrical case. However, the situation might be different in the case of the nonsymmetrical molecules such as tolylene 2,4-diisocyanate (TDI), XII. The reactivity of the two isocyanates in the monomer could differ considerably owing to steric effects. In addition to the steric effect, a proximity effect as indicated in eq 1 and 2 can further affect the reactivity. If such a situation exists, there must be four reactivity constants. The latter case is too difficult to be considered here, hence we shall be concerned only with a steric effect for the nonsymmetrical case.

In both cases, one has to be concerned with the definition of a hard block segment. In the simplified reaction scheme to be considered, only urethane groups are formed. Every prepolymer diol unit ends in a urethane group because the initial reaction between excess AA and BB is assumed to proceed until all B-type ends have reacted, at which point $X_1{}^0$ unreacted AA units remain. The extension reaction may be conducted with an excess of either AA or CC and may not go to complete reaction of available groups. Hence there may exist unreacted A- or C-type ends. The reacted A- or C-type ends also form only urethane groups.

With these restrictions the definition of a hard block segment can be considered. When a diisocyanate unit is sandwiched between two prepolymer units

$$\sim\!\!\sim\mathrm{AA}\sim\!\!\sim$$
type 1

where $\sim\!\!\sim$ represents a flexible prepolymer BB unit, it probably will not be involved in phase segregation, hence is considered part of the soft block segment.[3b] Similarly, the external segment type

$$\sim\!\!\sim\mathrm{AA}$$
type 2

is considered as part of the soft block segment, hence all units of the form $\mathrm{AA(BBAA)}_{n-1}$, where $n > 1$, are considered as soft segments. However, one can argue whether the internal segment type

$$\sim\!\!\sim\mathrm{AACCAA}\sim\!\!\sim$$
type 3

would be crystallizable; the choice may depend on the particular combination of diisocyanate and extender molecules chosen to form the segmented polyurethane. The next possible internal segment would be of the form

$$\sim\!\!\sim\mathrm{AACCX_1CCAA}\sim\!\!\sim$$
type 4, $s = 1$

where X_1 represents reacted diisocyanates that remained as unreacted monomer at the end of the AA–BB reaction, while AA represents diisocyanates that reacted at one end with a prepolymer unit during the AA–BB reaction. Larger internal segments can also be formed

$$\sim\!\!\sim\mathrm{AA(CCX_1)_sCCAA}\sim\!\!\sim$$
type 4

If segment type 3 is considered as part of the soft block, then there are exactly s X_1 units in the hard block segment type 4. This number is called the "counted unit" to avoid confusion with the usual term "repeat unit" because a variety of ways of counting the monomers in a hard block segment will be used. If segment type 3 is considered part of the hard block segment, then there are $s + 1$ reacted diisocyanates and $s + 1$ reacted extender molecules in segment type 4. Table II gives a summary of the segment types so far discussed and five more types that are also hard block segments. Model I is the designation when segment type 3 is considered soft and only the X_1 units are counted. Model II is the situation when segment type 3 is considered hard and the number of diisocyanate units are counted. In both of these models, unreacted diisocyanate monomer is considered as a hard block portion in order to simplify the mathematics. Model III is the situation when the number of extender units are counted in a hard segment. The only difference between models II and III is which unreacted monomer is counted as part of the hard block segments. At high conversion, under stoichiometric conditions, the concentration of unreacted monomer approaches zero, and the difference between models II and III vanishes. The importance of defining so many models will become apparent in the discussion.

Table II
Types of Segments Present in Segmented Polyurethanes, and Definition of Repeat Units in Hard Block Segments

	No. of counted units in a hard block segment Model		
Segment types	I[b]	II[c]	III[d]
(1) $\sim\!\!\sim\mathrm{AA}\sim\!\!\sim$[a]	0	0	0
(2) $\sim\!\!\sim\mathrm{AA}$	0	0	0
(3) $\sim\!\!\sim\mathrm{AACCAA}\sim\!\!\sim$	0	1	1
(4) $\sim\!\!\sim\mathrm{AA(CCX_1)_sCCAA}\sim\!\!\sim$	s	$s + 1$	$s + 1$
(5) $\sim\!\!\sim\mathrm{AA(CCX_1)_s}$	s	s	s
(6) $\sim\!\!\sim\mathrm{AA(CCX_1)_sCC}$	s	$s + 1$	$s + 1$
(7) $\mathrm{X_1(CCX_1)_s}$	$s + 1$	$s + 1$	s
(8) $\mathrm{(CCX_1)_s}$	s	s	s
(9) $\mathrm{(CCX_1)_sCC}$	s	s	$s + 1$

[a] $\sim\!\!\sim$ represents a prepolymer segment. [b] The unit that is being counted is a diisocyanate residue X_1 derived from unreacted monomer remaining after the AA–BB reaction. [c] The counted unit is X_1 plus one isocyanate unit from each soft block segment unless it is segment type 5. [d] The counted unit is an extender molecule.

With these definitions of the symmetrical and nonsymmetrical cases and the various models of the hard block segment, we may proceed to consider the amount of unreacted diisocyanate at the end of the AA–BB reaction and the distribution of repeat units in a hard block segment under the following assumptions: (1) the reactivity of one end of a symmetrical diisocyanate monomer depends only on whether or not the other end has reacted; (2) the reaction between a diisocyanate and a diol is irreversible; (3) if one of the diisocyanate ends has reacted, whether the monomer is symmetrical or not, the reactivity of the unreacted end is independent of the molecular weight of the polymer to which it is attached; (4) the extender is a low molecular weight diol; (5) the reactivity of any hydroxyl group is independent of molecular weight; and (6) no other reactions occur. Because the derivations require great attention to detail, which is not required to follow the discussion, the results and their implications will be presented now. The derivations are in the appendices.

Results and Discussion

Equations A34, A48, A51, A55, A58, A61, and A64 for the symmetrical case, model I, and B9–B11 for the nonsymmetrical case, model I, were solved on an IBM 1130 computer by the RKGS subroutine given in the Scientific Subroutine

Table III
Values of X_1^0, Unreacted Monomer at the End of the AA–BB Reaction for the Symmetrical Case

Reactivity ratio[a] $\mu = k'/k$	Initial concentration of A_1[b] 2	3	4	5	6
1/3	0.713	1.565	2.471	3.404	4.356
1	0.500	1.333	2.250	3.200	4.167
3	0.306	1.159	2.108	3.081	4.065
12	0.139	1.049	2.031	3.022	4.018
36	0.066	1.017	2.011	3.008	4.006
∞	0	1.000	2.000	3.000	4.000

[a] The rate of the polymer reaction, k, differs from that of the monomer, k'. [b] B_1 = 1 mol/l., $C_1 = A_1 - B_1$. These are defined as stoichiometric conditions.

Table IV
Values of X_1^0, Unreacted Monomer at the End of the AA–BB Reaction for the Nonsymmetrical Case

μ[a]	Initial concentration of A_1[b] 2	3	4	5	6
3	0.434	1.274	2.200	3.158	4.130
12	0.251	1.129	2.088	3.067	4.054
36	0.132	1.053	2.035	3.026	4.021
∞	0	1.000	2.000	3.000	4.000

[a] The initial rate constants of monomer are different. [b] Stoichiometric conditions.

Package (see paragraph at end of paper regarding supplementary material).[11] The program also computed values of conversion; unreacted diisocyanate monomer; unreacted extender; the number average number of diisocynaate molecules in a hard block segment, $\bar{s}$; the number average molecular wieght, $\bar{M}_T$; and the number of monomer units per polymer molecule, $\bar{m}_T$. Analytical solutions can be obtained for models II and III.

Tables III and IV give the values of X_1^0 for a variety of μ and A_1 values and with B_1 = 1 mol/l. and $C_1 = A_1 - B_1$. For the symmetrical case, X_1^0 decreases with increasing μ, approaching the limit $A_1 - 2B_1$ as μ approaches infinity or as A_1 increases. If the value of μ is less than unity (that is, polymeric A-type ends react faster than the monomeric A-type ends) the result of the AA–BB reaction is a high molecular weight oligomer with a large excess of unreacted monomer, as predicted in the introduction.

For the nonsymmetrical case (Table IV) values of X_1^0 for $\mu = 1/3$ are equivalent to those for $\mu = 3$ because it makes no difference if the A^0 end of a diisocyanate monomer of the form A^0A' is three times faster than the A′ end or if it is three times slower than the A′ end. Values of X_1^0 for $\mu = 1$ are identical with those given in Table III. The X_1^0 values for the nonsymmetrical case do not decrease as rapidly with increasing μ as in the symmetrical case but still approach the limit $A_1 - 2B_1$ at high values of μ or A_1.

The number average molecular weight for the extended polymer is computed by assuming molecular weight values of 250 for AA, equivalent to MDI, OCN-Ph-CH$_2$-Ph-NCO; 2000 for BB, a common value of commercial material for either a polyester or a polyether; and 90 for CC, equivalent to butanediol. Table V gives the values for the symmetrical case at 0, 95, and 99% conversion.

The initial values are consistent with the concentration of unreacted monomer; high molecular weight oligomers result in more unreacted monomer. As the ratio of A_1/B_1 is increased, the molecular weight drops, owing to the increased amount of monomer to compete with the partially formed oligomer. At high values of μ, the oligomer is primarily composed of one unit of prepolymer capped with two units of diisocyanate monomer.

At 95 and 99% conversion, there is little change in $\bar{M}_T$ or $\bar{m}_T$ with increasing μ. The primary difference among $\mu = 1/3$, 1, and the rest is due to small amounts of unreacted diisocyanate remaining in the mixture. There is essentially no unreacted diisocyanate at higher values of μ. The decrease in $\bar{M}_T$ and $\bar{m}_T$ with increasing A_1 is due in part to the increased molar concentration of the low molecular weight monomers relative to the high molecular weight prepolymer and in part to a lower value of $\bar{m}_T$ at the start of the extending reaction.

Table VI presents the number average molecular weight and degree of polymerization of oligomer at 0% conversion for the nonsymmetrical case. The differences between the entries in Table VI *vs.* Table V are due to the differences in X_1^0. Values of the parameters at 95 and 99% conversion should agree closely with those in Table V because the values of unreacted diisocyanate and extender are almost identical.

The number average number of diisocyanate molecules in the hard block segments, $\bar{s}$, is given in Table VII for the symmetrical case, model I, and in Table VIII for the nonsymmetrical case, model I, both at 95, 99, and 100% conversion. As conversion increases, $\bar{s}$ increases, not because of the depletion of unreacted monomer but because of the coupling of preformed sequences to make longer sequences. The nonsymmetrical case gives slightly higher values for $\bar{s}$, owing to the higher values of X_1^0. Both cases tend toward an $\bar{s}$ of $(A_1 - B_1)/B_1$ as μ becomes large, but $\bar{s}$ equals A_1/B_1 when $\mu = 1$ at 100% conversion. Several authors have assumed that $\bar{s}$ is equal to $A_1 - B_1$ when $B_1 = 1$, based on a simple stoichiometric approach. This value is called the "ideal" case in Tables VII and VIII.

In models II and III for both the symmetrical and nonsymmetrical cases, $\bar{s}$ under stoichiometric conditions at 100% conversion gives

$$\bar{s} = C_1/(C_1 - X_1^0) \tag{3}$$

Substitution of X_1^0 obtained from Tables III and IV into eq 3, recalling that $C_1 = A_1 - B_1$, yields exactly the values $\bar{s}$ given in Tables VII and VIII at 100% conversion! This remarkable outcome must be due to the distribution of the monomers that make up the hard block segment. Reference to Table II shows that model I counts the X_1 units, which, except for segment types 5, 7, and 8, are exactly the number of CC units less one. At 100% conversion, only one molecule of infinite molecular weight remains which contains only segment type 4 groups. The number average number of extender molecules per hard block segment is independent of whether one counts all of the extender molecules per segment or all of the extender molecules less one per segment.

Let $G(s)$ be the concentration of all extender molecules per hard block segment and

$$\sum_{s=1}^{\infty} sG(s) = C_1 \tag{4}$$

also

$$\bar{s} = C_1 / \sum_{s=1}^{\infty} G(s) \tag{5}$$

Table V
Number Average Molecular Weight and Degree of Polymerization of "Polymer" as a Function of the Extending Reaction for the Symmetrical Case (see eq A23–26) Assuming Molecular Weight Values of 250 for AA, 2000 for BB, and 90 for CC

	Initial concentration of A				
μ	2	3	4	5	6
			0% Conversion		
$\frac{1}{3}$	8083 7.97	5427 5.60	4505 4.78	4031 4.36	3740 4.10
1	4750 5.00	3625 4.00	3250 3.67	3062 3.50	2950 3.40
3	3492 3.88	2926 3.38	2772 3.24	2699 3.18	2657 3.14
12	2862 3.32	2616 3.10	2571 3.07	2551 3.04	2540 3.04
36	2660 3.14	2540 3.03	2524 3.02	2517 3.02	2513 3.01
			95% Conversion		
$\frac{1}{3}$	36,400 55.9	20,600 42.0	15,300 37.3	12,700 35.0	11,110 33.6
1	26,900 41.5	15,300 31.2	11,400 27.8	9,450 26.1	8,270 25.1
3	26,400 41.0	15,030 30.7	11,200 27.3	9,260 25.6	8,100 24.5
12	26,400 41.0	15,030 30.7	11,200 27.3	9,260 25.6	8,100 24.5
36	26,400 41.0	15,030 30.7	11,200 27.3	9,260 25.6	8,100 24.5
			99% Conversion		
$\frac{1}{3}$	175,000 270.7	99,400 203.2	73,900 180.7	61,200 169.5	53,600 162.7
1	131,000 201.7	73,950 151.4	55,000 134.6	45,600 126.4	39,900 121.2
3	130,000 201.2	73,700 150.9	54,800 134.1	45,500 125.9	39,700 120.7
12	130,000 201.2	73,700 150.9	54,800 134.1	45,400 125.7	39,700 120.7
36	130,000 201.2	73,700 150.9	54,800 134.1	45,400 125.7	39,700 120.7

In order to meet the criterion that the same $\bar{s}$ is obtained when $s - 1$, $s \geq 2$ is used to count the number of extender molecules per hard block segment instead of s, the following equation must be true.

$$\bar{s} = \sum_{s=2}^{\infty} G(s) \Big/ \sum_{s=2}^{\infty} (s - 1)G(s) \tag{6}$$

This result immediately implies

$$\sum_{s=1}^{\infty} G(s) = \kappa \sum_{s=2}^{\infty} G(s) \tag{7}$$

and

$$\sum_{s=1}^{\infty} sG(s) = \kappa \sum_{s=2}^{\infty} (s - 1)G(s) \tag{8}$$

where κ is a constant. Examination of the distributions in common use in macromolecular chemistry found in ref 12 reveals that only the most probable distribution conforms to eq 7 and 8. Thus

$$F(r) = (1 - p)p^{r-1} = G(s) \Big/ \sum_{s=1}^{\infty} G(s) \tag{9}$$

$$\sum_{r=a}^{\infty} F(r) = p^{a-1} \tag{10}$$

$$\sum_{r=a}^{\infty} (r + 1 - a)F(r) = p^{a-1}/(1 - p) \tag{11}$$

$$\sum_{r=a}^{\infty} (r + 1 - a)^2 F(r) = p^{a-1}(1 + p)/(1 - p) \tag{12}$$

where $a = 1, 2, 3$, etc.

Hence the distribution of extender molecules in the hard block segment must conform to the most probable distribution. The weight average number of extender molecules per hard block segment is then

$$\bar{s}_w = (1 + p)/(1 - p) \tag{13}$$

Table VI
Number Average Molecular Weight and Degree of Polymerization of "Polymer" as a Function of the Extending Reaction for the Nonsymmetrical Case[a]

	Initial concentration of A_1				
μ	2	3	4	5	6
3	4225	3349	3063	2922	2837
	4.53	3.75	3.50	3.37	3.30
12	3254	2833	2717	2661	2628
	3.67	3.30	3.19	3.14	3.11
36	2842	2626	2582	2560	2547
	3.30	3.11	3.07	3.05	3.04

[a] Same values of molecular weight of monomers and prepolymers as in Table V.

Table VII
Number Average Length of Hard Block Segments as a Function of Initial Concentration, Conversion, and Reactivity Ratio for the Symmetrical Case, Model I (see also Figure 1)

	Initial concentration of A_1				
μ	2	3	4	5	6
			95% Conversion		
$\frac{1}{3}$	2.63	3.21	3.69	4.09	4.45
1	1.82	2.51	3.10	3.60	4.03
3	1.40	2.15	2.82	3.39	3.88
12	1.15	1.96	2.67	3.28	3.80
36	1.07	1.90	2.63	3.25	3.78
			99% Conversion		
$\frac{1}{3}$	3.26	4.22	5.10	5.93	6.73
1	1.96	2.89	3.77	4.63	5.46
3	1.43	2.33	3.24	4.12	4.97
12	1.16	2.07	3.00	3.90	4.76
36	1.07	2.01	2.94	3.84	4.71
			100% Conversion		
$\frac{1}{3}$	3.48	4.60	5.60	6.71	7.76
1	2.00	3.00	4.00	5.00	6.00
3	1.44	2.38	3.36	4.35	5.35
12	1.16	2.10	3.10	4.09	5.09
36	1.07	2.03	3.04	4.03	5.03
Ideal	1.00	2.00	3.00	4.00	5.00

and the heterogeneity index is

$$\bar{s}_w/\bar{s} = 1 + p = 1 + X_1^0/C_1 \qquad (14)$$

Because the parameter p is not close to unity, the ratio of weight to number average sequence length is not equal to 2. Calculated values of the heterogeneity index are given in Tables IX and X for the symmetric and nonsymmetric cases. The distribution is narrower for low values of A_1 and high values of μ, that is, conditions which favor low values of X_1^0.

The value of $\bar{s}$ for models II and III for either the symmetrical or the nonsymmetrical case as a function of conversion can be obtained easily. Figure 1 shows the dependence of $\bar{s}$ as a function of conversion for the symmetrical case with $\mu = \frac{1}{3}$ or 36 under stoichiometric conditions for the different models. The length of the hard block segment is more difficult to control at large values of A_1 and at small values of μ. Because the various models of the hard block segments give essentially the same $\bar{s}$ values, there is little departure, if any, from the most probable distribution in the range of 95–100% conversion. Similar conclusions can be obtained from an examination of $\bar{s}$ as a function of conversion for the nonsymmetrical case, model I, Table VIII. Models II and III differ from model I (Table XI) by even smaller amounts than in the symmetrical case.

Examination of Tables VII and VIII at 100% conversion immediately shows that $\bar{s}$ is larger than that for the ideal case where μ is finite. This means that properties which depend upon the hard block length will show this dependence at lower values of the A_1/B_1 ratio than predicted by the ideal case. In the two-stage polymerization considered thus

Table VIII
Number Average Length of Hard Block Segments as a Function of Initial Concentration, Conversion, and Reactivity Ratio for the Nonsymmetrical Case, Model I

	Initial concentration of A_1				
μ	2	3	4	5	6
			95% Conversion		
3	1.67	2.41	3.04	3.57	4.04
12	1.31	2.10	2.80	3.38	3.89
36	1.14	1.97	2.68	3.30	3.82
			99% Conversion		
3	1.75	2.68	3.58	4.45	5.30
12	1.33	2.25	3.18	4.07	4.93
36	1.15	2.08	3.01	3.91	4.78
			100% Conversion		
3	1.77	2.75	3.75	4.75	5.75
12	1.34	2.30	3.29	4.29	5.29
36	1.15	2.11	3.11	4.11	5.11
Ideal	1.00	2.00	3.00	4.00	5.00

Table IX
Heterogeneity Index, $\bar{s}_w/\bar{s}$, for the Symmetrical Case at 100% Conversion

	Initial concentration of A_1				
μ	2	3	4	5	6
$\frac{1}{3}$	1.71	1.78	1.82	1.85	1.87
1	1.50	1.67	1.75	1.80	1.83
3	1.31	1.58	1.70	1.77	1.81
12	1.14	1.52	1.68	1.76	1.80
36	1.07	1.51	1.67	1.75	1.80

Table X
Heterogeneity Index for the Nonsymmetrical Case at 100% Conversion

	Initial concentration of A_1				
μ	2	3	4	5	6
1	1.50	1.69	1.75	1.80	1.83
3	1.43	1.64	1.73	1.79	1.83
12	1.25	1.56	1.70	1.77	1.81
36	1.13	1.53	1.68	1.76	1.80

Table XI
Total Number and Internal Number of Hard Block Sequences per Polymer Molecule for the Symmetrical Case, Model I

	Initial concentration of A									
	2		3		4		5		6	
μ	Total	Internal	Total	Internal	Total	Internal	Total	Internal	Total	Internal
					95% Conversion					
⅓	3.82	2.07	3.45	1.63	3.17	1.32	2.95	1.10	2.78	0.93
1	2.85	1.93	2.77	1.58	2.53	1.24	2.33	0.98	2.17	0.80
3	2.24	1.75	2.76	1.82	2.56	1.42	2.33	1.11	2.15	0.88
12	1.24	1.03	2.75	1.93	2.60	1.52	2.36	1.18	2.17	0.93
36	0.64	0.54	2.74	1.95	2.61	1.56	2.37	1.20	2.17	0.94
					99% Conversion					
⅓	14.81	12.92	12.58	10.60	10.96	8.93	10.84	8.55	8.80	6.73
1	12.86	11.84	11.66	10.36	10.03	8.58	8.73	7.19	7.71	6.13
3	10.75	10.24	12.52	11.51	10.92	9.67	9.42	8.04	8.23	6.77
12	6.02	5.81	12.74	11.86	11.35	10.18	9.77	8.44	8.49	7.06
36	4.20	4.07	12.75	11.91	11.44	10.31	9.85	8.54	8.55	7.14

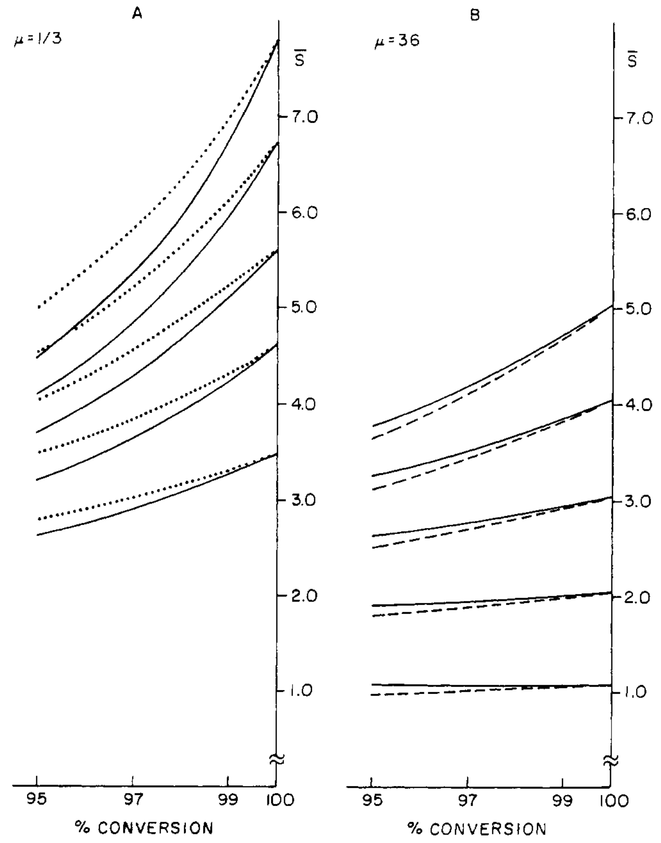


Figure 1. The number average number of counted units in a hard block segment, $\bar{s}$, as a function of conversion for the symmetrical case when $\mu = \frac{1}{3}$ and $\mu = 36$, under stoichiometric conditions, $B_1 = 1$ mol/l., $A_1 = 2, 3, 4, 5$, and 6 mol/l. in ascending order. For $\mu = \frac{1}{3}$: $\bar{s}^{\mathrm{I}} = \bar{s}^{\mathrm{II}}$ (——) and $\bar{s}^{\mathrm{III}}$ (· · ·). For $\mu = 36$: $\bar{s}^{\mathrm{I}} = \bar{s}^{\mathrm{III}}$ (——) and $\bar{s}^{\mathrm{II}}$ (- - -). The method of counting the units varies among cases I, II, and III.

far, on increasing the ratio A_1/B_1 to obtain longer hard block segments, the molecular weight of the resultant extended polymer is reduced. Can a recipe be found in which the average hard block length is varied while maintaining the molecular weight reasonably constant? One method would be to react varying amounts of diisocyanate monomer, A_2, with an excess amount of extender, C_2, to form an oligomer of the form $\mathrm{CC(AACC)}_t$. This mixture can then be combined with the reaction mixture from the $\mathrm{A_1}$–$\mathrm{B_1}$ reaction to form the final polymer. This scheme has been incorporated into the computer program to allow one to calculate the number average molecular weight and the number average length of the hard block segments under a variety of polymerization conditions. In general, if $\bar{s}$ depends on conversion in the two-step synthesis, the dependence is increased in the three-step synthesis. On the other hand, at low values of total diisocyanate concentration, long sequence lengths should be able to be produced.

An alternative method of forming a segmented block copolymer is to combine all three reactants simultaneously in a one-stage polymerization. For the most general case one can write

$$\mathrm{AA + BB} \xrightarrow{\mu k} \mathrm{AABB}$$

$$\mathrm{AABB + BB} \xrightarrow{k} \mathrm{BBAABB}$$

$$\mathrm{AA + CC} \xrightarrow{\mu\nu k} \mathrm{AACC}$$

$$\mathrm{AACC + CC} \xrightarrow{\nu k} \mathrm{CCAACC}$$

That is, the first reaction of the monomer AA with BB in the symmetrical case has a specific rate constant μk, while the rate of AA with CC is $\mu\nu k$. The specific rate constant for a polymer chain with an A-type end reacting with a B-type end is k, while that reacting with a C-type end is νk. The value of ν probably is different from unity; see Table I. Appendix C gives the derivation for $\bar{s}$ for the limiting case when $\nu = 1$. At 100% conversion under stoichiometric conditions

$$\bar{s} = A_1/B_1 \tag{15}$$

which is independent of μ and equal to the two-stage process when $\mu = 1$. Of course, as ν departs from unity, deviations from eq 15 will occur.

The nonlinear increase in $\bar{s}$ as a function of conversion at low values of μ and high values of A_1 shown in Figure 1 is caused by coupling of hard block segment types 5–9 in Table II in the final steps of conversion. The total concentration of hard block segments is given by $\Sigma g(s)^{\mathrm{I}}$, while the

APPENDIX A

Detailed Derivation of Equations for the Symmetrical Case

The reactions of the diisocyanate (AA) with the prepolymer diol (BB) may be specified.

$$AA + BB \xrightarrow{k'} AABB \tag{A1}$$

$$AABB + BB \xrightarrow{k'} BBAABB \tag{A2}$$

After completion of the reaction of BB with excess AA, the resultant prepolymer is extended with CC, where CC is a diol. The absolute reactivity of AA with CC may be different from that with BB, but the relative reactivity $\mu = k'/k$ is independent of whether AA is reacting with BB or CC. Upon addition of AA to BB, molecules of the following form are created and destroyed while the reaction is proceeding:

x_n molecules containing two terminal A units, and a total of $\underline{n}$ AA units, $\underline{n}$-1 BB units.
x_1 = the amount of unreacted AA units.

y_n molecules containing one terminal A unit and one terminal B unit, and a total of $\underline{n}$ AA units and $\underline{n}$ BB units.

z_n molecules containing two terminal B units and a total of $\underline{n}$ AA units and $\underline{n}$ + 1 BB units.
z_0 = the amount of unreacted BB units.

The x-type molecules can react with the y-type molecules in two ways (either end of an x-type reacts with only one end of a y-type) and with a z-type molecules in 4 ways. A y-type molecule can react with itself and with a z-type molecule in two ways. The rate constants k and k'

need not be invarient with time; they can vary with viscosity, temperature or extent of conversion provided that the ratio $\mu = k'/k$ remains constant throughout the reaction. To allow for a variation of k with time, we introduce the variable -

$$t = \int_0^{\tau} k\,d\tau \tag{A3}$$

The kinetic equations are:

$$dx_1/dt = -2\mu x_1(S + 2T) \tag{A4}$$

$$dx_n/dt = 2\mu x_1 y_{n-1} + 2\sum_{i=2}^{n-1} x_i y_{n-i} - 2x_n(S + 2T), \quad (n>1) \tag{A5}$$

$$dy_n/dt = \frac{2}{2}\sum_{i=1}^{n-1} y_i y_{n-i} + 4\mu x_1 z_{n-1} + 4\sum_{i=2}^{n-1} x_i z_{n-1} - 2y_n\,[R + S + T + (\mu-1)x_1] \tag{A6}$$

$$dz_n/dt = 2\sum_{i=1}^{n} y_i z_{n-1} - 2z_n\,[S + 2R + 2(\mu-1)x_1] \tag{A7}$$

where

$$R = \sum_{n=1}^{\infty} x_n, \quad S = \sum_{n=1}^{\infty} y_n, \quad T = \sum_{n=0}^{\infty} z_n \tag{A8}$$

Note that the coefficient before the first term on the right hand side of equation A6 is unity because although a y-type molecule can react with itself in two ways, the summation will count each item twice. The $(\mu-1)x_1$ term must be added to $\underline{\underline{R}}$ to account for the different reactivity of x_1 from the other x_n.

The mass balance of the various terms requires that

$$\sum_{n=1}^{\infty} (nx_n + ny_n + nz_n) = A_1 \tag{A9}$$

$$\sum_{n=1}^{\infty} [(n-1)x_n + ny_n + (n+1)z_n] = B_1 \tag{A10}$$

Subtraction of equation A10 from A9 shows that

$$R - T = A_1 - B_1 = \text{constant} = -f' \tag{A11}$$

because each B-type end that reacts also removes an A-type end, hence the stoichiometric difference remains constant. Therefore

$$dR/dt = dT/dt \tag{A12}$$

We can now sum equations A6 and A 7

$$\begin{aligned} dT/dt &= -4(\mu-1)x_1T - 4RT \\ &= -4(\mu-1)x_1T - 4T(T-f') \end{aligned} \tag{A13}$$

$$dS/dt = S^2 + 4T(T-f') + 2(\mu-1)x_1\,(2T+S) - 2S(S+2T-f') \tag{A14}$$

Now let

$$Q = S + 2T \tag{A15}$$

Note that Q is the total number of unreacted B-type groups. Also $Q-2f'$ is the number of unreacted A-type groups. By adding twice equation A13 to equation A14 we find

$$dQ/dt = -Q^2 + 2f'Q - 2(\mu-1)x_1Q \tag{A16}$$

$$dx_1/dt = -2\mu x_1 Q \tag{A17}$$

Now x_1 can be found as a function of Q

$$dQ/dx_1 = Q/2\mu x_1 - f'/\mu x_1 + 1 - 1/\mu \tag{A18}$$

which integrates to

$$(2\mu-1)Q = 2(\mu-1)x_1 + 2(2\mu-1)f' + Cx_1^{1/2\mu} \tag{A19}$$

where C is an integration constant. At the start of the reaction $x_1 = A_1$, $Q = 2B_1$, hence C can be evaluated. The result is

$$(2\mu-1)Q/2A_1 = \mu(x_1/A_1)^{1/2\mu} + (\mu-1)(x_1/A_1) - (2\mu-1)(A_1-B_1)/A_1 \tag{A20}$$

Because we specified that $A_1 > B_1$, the value of Q is zero at infinite time. Therefore the final value X_1^0 of x_1 can be found from the relation

$$\mu(X_1^0/A_1)^{1/2\mu} + (\mu-1)(X_1^0/A_1) = (2\mu-1)(A_1-B_1)/A_1 \tag{A21}$$

If $\mu = 1$, that is, all A-type ends have the same reactivity, then

$$X_1^0 = (A_1-B_1)^2/A_1 \tag{A22}$$

which can be derived by straightforward statistical methods.

The number average molecular weight of the oligomer produced at the end of the AA-BB reaction, $\bar{M}_s$ can be easily found. Let M_A, $\bar{M}_B$ be the molecular weights of the AA and BB molecules, respectively. Since BB is either a polyester or a polyether, $\bar{M}_B$ is the number average molecular

weight of BB. The original number of moles is $(A_1 + B_1)\underline{V}$ where V is the volume of the reacting system and if BB reacts completely, the final number of moles is $(A_1 - B_1)V$. Hence, the number of soft segment or oligomer moles is $(A_1 - B_1 - X_1^0)\underline{V}$ and

$$\bar{M}_s = \left[(A_1-X_1^0)M_A + B_1\bar{M}_B\right] / (A_1-B_1-X_1^0) \tag{A23}$$

Because the molecular weight of B may exceed that of A by a factor of 10, we may also calculate the total number of monomers per oligomer molecule, $\bar{m}_s$

$$\bar{m}_s = (A_1-X_1^0 + B_1)/(A_1-B_1-X_1^0) \tag{A24}$$

Note that $\bar{m}_s$ is not based on the average number of repeat units per oligomer molecule, but rather on the average number of monomers per oligomer. Thus, the number of monomers in AABBAABBAA is five even though this unit is sometimes called a trimer.

During the extending reaction, the number of unreacted A-ends is $(\gamma-2f)\underline{V}$, the number of unreacted C-ends is $\gamma\underline{V}$, hence, the total number of molecules is $(2\gamma-2f)\underline{V}/2$ while the number of polymer molecules is $(\gamma-f-X_1-w_1)\underline{V}$, where γ is the total number of C-type ends, f is the molar excess of diol molecules over diisocyanate molecules, and w_1 is the unreacted extender, hence the number average molecular weight of the extended polymer, $\bar{M}_T$, is

$$\bar{M}_T = \frac{(A_1-X_1)M_A + B_1\bar{M}_B + \left[C_1 - w_1\right]M_C}{\gamma - \left[f + X_1 + w_1\right]} \tag{A25}$$

If f=0, that is $C_1 = A_1-B_1$, $\bar{M}_T$ cannot be evaluated at complete reaction because only one molecule of infinite molecular weight remains. Therefore, $\bar{M}_T$ must be evaluated under conditions close to, but not completely reacted.

The number of monomers per polymer molecule is

$$\bar{m}_T = \left[A_1-X_1 + B_1 + C_1 - w_1\right] / \left[\gamma - (f + X_1 + w_1)\right] \tag{A26}$$

We now wish to extend the reaction by addition of a low molecular weight extender (CC). This reaction results in molecules of the type

u(n,r) concentration of molecules containing two terminal A-type units, $\underline{n}$ AA units, $\underline{m}$ BB units and $\underline{r}$ CC units, where $m = n-r-1$, $0 \le r \le n-1$. $u(n,0) = x_n$, $u(1,0) = X_1$.

v(n,r) concentration of molecules containing one terminal A unit and one terminal C unit, $\underline{n}$ AA units, $\underline{m}$ BB units, and $\underline{r}$ CC units where $m = n-r$, and $0 \le r \le n$.

w(n,r) concentration of molecules containing two terminal C units, $\underline{n}$ AA units, $\underline{m}$ BB units, and $\underline{r}$ CC units where $m = n-r+1$, $1 \le r \le n+1$, and

$w_1 = w(0,1)$ is the concentration of unreacted CC units.

We wish to know the sequence length distribution of X_1 (where X_1 represents the unreacted AA units) reacting only with CC to form sequences of the type $X_1(CCX_1)_{s-1}$ as these sequences form the "hard" or crystallizable portions of the final polymer in Model I. The sequences $X_1(CCX_1)_{s-1}$ can exist as internal pieces inside molecules, as a terminal sequence of a molecule, or as independent entities containing terminal A or C units as described in Table 2.

For Model I, define $g(s)^I$ equal to the total concentration of the following six sequences described in Table 2.

$$g(s)^I = [\cdots x_nCC(X_1CC)_s x_m \cdots] + [\cdots x_nCC(X_1CC)_s] + [\cdots x_n(CCX_1)_s] + [u(s,s-1)] + [v(s,s)] + [w(s,s+1)],\ n,m \neq 0,1 \tag{A27}$$

The definition of $[\ \ x_nCC(X_1CC)_s x_m\ \ ]$ $n,m \neq 0,1$ is the total concentration of units containing a sequence of s X_1 units where both ends of the sequence are capped by x_n, $n \neq 1$, units. There may be several hard block segments within a given u-, v-, or w-type molecule. With this definition, $\sum_{s=1}^{\infty} g(s)^I$ is the total number of sequences and $\Sigma s g(s)^I = X_1^0$. The number average number of X_1's in a sequence is just $X_1^0/\Sigma g(s)^I \equiv \bar{S}$.

The kinetic scheme for the reaction is given in Scheme I:

$$\begin{array}{lclcll}
X_1 & + & w(n,r) & \xrightarrow{k'} & v(n+1,r) & 4 \\
X_1 & + & v(n,r) & \xrightarrow{k'} & u(n+1,r) & 2 \\
u(n,q) & + & w(m,r) & \xrightarrow{k} & v(n+m,q+r) & 4 \quad n \neq 1 \\
u(n,q) & + & v(m,r) & \xrightarrow{k} & u(n+m,q+r) & 2 \quad n \neq 1 \\
v(n,q) & + & v(m,r) & \xrightarrow{k} & v(n+m,q+r) & 2 \\
v(n,q) & + & w(m,r) & \xrightarrow{k} & w(n+m,q+r) & 2
\end{array}$$

Scheme I

where the number of ways two specified molecules can react to form a specified product is given in the right hand column. A given product, however, can be formed by a large variety of initial reactants.

The total number of C-ends at any time t is given by

$$\gamma = V + 2W = \sum_{\substack{n=1 \\ r=1,\,r\le n}}^{\infty} v(n,r) + 2\sum_{\substack{n=0 \\ r=1,\,r\le n+1}}^{\infty} w(n,r) \tag{A28}$$

where t is given by equation A3.

For the following treatment to be valid it is necessary that the ratio $\mu = k'/k$ remain constant throughout the reaction.

We can show that

$$d\gamma/dt = -2(\mu-1)X_1\,\gamma + 2\gamma f - \gamma^2 \tag{A29}$$

where

$$f = C_1 - (A_1 - B_1) \tag{A30}$$

The total concentration of A-type end groups is

$$\alpha = 2U + V = 2X_1 + 2\sum_{n=2}^{\infty}\sum_{r=0}^{\infty} u(n,r) + \sum_{n=1}^{\infty}\sum_{r=1}^{\infty} v(n,r) \tag{A31}$$

The mass balance condition requires

$$d\alpha/dt = d\gamma/dt \tag{A32}$$

hence

$$\alpha = \gamma - 2f \tag{A33}$$

The equation for X_1 is

$$dX_1/dt = -2\mu X_1\gamma \tag{A34}$$

An equation similar to equation A21 can be found for the concentration of X_1 as a function of γ:

$$(2\mu-1)\gamma = 2(\mu-1)X_1 + 2(2\mu-1)f + \left[(2\mu-1)\gamma^0 - 2(\mu-1)X_1^0 - 2(2\mu-1)f\right]\left[\frac{X_1}{X_1^0}\right]^{1/2\mu} \tag{A35}$$

However, as will be seen, it is easier to use the differential form, equation A34.

To determine the concentration of the components of $g(s)^I$ we need to determine the total number of "active" and "inactive" terminal ends of the u-, v-, and w-type molecules. We define an active X-end as that type of molecule which on reaction with an active C-end, extends the sequence length $\underline{s}$. Thus the following molecules contain active X-ends:

$$\cdots x_n(CCX_1)_s \qquad n \neq 0,\ 1$$

$$v(s,s)$$

$$u(s,s-1)$$

The total concentration of active X-ends is:

$$G^* = \sum_{s=1}^{\infty}\left[\cdots x_n(CCX_1)_s\right] + \sum_{s=1}^{\infty} v(s,s) + 2\sum_{s=1}^{\infty} u(s,s-1) \tag{A36}$$

$$G^* = H^* + V^* + 2U^* \tag{A37}$$

where
$$H^* = \sum_{s=1}^{\infty}\left[\cdots x_n(CCX_1)_s\right] \qquad n \neq 0,\ 1 \tag{A38}$$

$$V^* = \sum_{s=1}^{\infty} v(s,s) \tag{A39}$$

$$U^* = \sum_{s=1}^{\infty} u(s,s-1) \tag{A40}$$

The concentration of inactive A-type ends is

$$\beta = \gamma - G^* \tag{A41}$$

On the other hand, the total concentration of active <u>C</u> ends is

$$G^{**} = H^{**} + V^* + 2W^* - 2w_1 \tag{A42}$$

where
$$H^{**} = \sum_{s=1}^{\infty}\left[\cdots x_nCC(X_1CC)_s\right] \qquad n \neq 0,\ 1 \tag{A43}$$

$$W^* = \sum_{s=0}^{\infty} w(s,s+1) \tag{A44}$$

Note that G^{**} does not contain unreacted CC as it is not

connected to an X_1.

The concentration of inactive C-type end groups attached to polymer chains is

$$\delta = \gamma - G^{**} - 2w_1 \tag{A45}$$

The differential equations for the rate of formation of all terms and their summations can be easily written from the kinetic scheme; presented here are the ones required to evaluate $\Sigma g(s)$

$$dX_1/dt = -2\mu X_1\gamma = -2\mu u(1,0)\gamma \tag{A46}$$

$$du(s,s-1)/dt = 2\sum_{i=1}^{s-1} u(i,i-1)v(s-i,s-i) + 2(\mu-1)X_1v(s-1,s-1) - 2u(s,s-1)\gamma \tag{A47}$$

Summing equation A47 from s = 1 to infinity gives

$$dU^*/dt = 2\left[U^* + (\mu-1)X_1\right](V^* - \gamma) \tag{A48}$$

Now

$$dv(1,1)/dt = 4\mu X_1w_1 - \left[\alpha + 2(\mu-1)X_1 + \gamma\right]v(1,1) \tag{A49}$$

$$dv(s,s)/dt = 4(\mu-1)X_1w(s-1,s) + 4\sum_{i=1}^{s} u(i,i-1)w(s-i,s-i+1) + \sum_{i=1}^{s} v(i,i)v(i,i) - \left[\alpha + 2(\mu-1)X_1 + \gamma\right]v(s,s) \tag{A50}$$

Summation from s=1 to ∞ yields

$$dV^*/dt = 4W^*\left[U^* + (\mu-1)X_1\right] + V^*V^* - 2V^*\left[\gamma - f + (\mu-1)X_1\right] \tag{A51}$$

$$dw_1/dt = -2\left[\alpha + 2(\mu-1)X_1\right]w_1 \tag{A52}$$

which with the aid of equation A29 integrates to

$$w_1 = \gamma^2/4C_1 \tag{A53}$$

$$\frac{dw(s,s+1)}{dt} = 2\sum_{i=0}^{s-1} w(i,i+1)v(s-i,s-i) - 2\left[\gamma - 2f + 2(\mu-1)X_1\right]w(s,s+1) \tag{A54}$$

Summation from s=0 to ∞ yields

$$dW^*/dt = 2V^*W^* - 2W^*\left[\gamma - 2f + 2(\mu-1)X_1\right] \tag{A55}$$

Also from kinetic scheme, we can write the differential equation for

$$h(s)^* = \left[\cdots x_n(CCX_1)_s\right] \qquad n \neq 0,1$$

and

$$h(s)^{**} = \left[\cdots x_n(CCX_1)_s\right] \qquad n \neq 0,1$$

$$\frac{dh(s)^*}{dt} = \beta v(s,s) + 2\delta u(s,s-1) + \sum_{i=1}^{s-1} h(i)^*v(s-i,s-i) + 2\sum_{i=1}^{s-1} h(i)^{**}u(s-i,s-i-1) - h(s)^*\gamma \tag{A56}$$

$$dH^*/dt = \beta V^* + 2\delta\tilde{U} + H^*V^* - 2H^{**}\tilde{U} - H^*\gamma \tag{A57}$$

where $\tilde{U} = U^* + (\mu-1)X_1$

Substitution of equations A41, A45, A57, A37 and A42 into the differential form of equation A37 yields

$$dG^*/dt = -\left[G^* + 2(\mu-1)X_1\right]\gamma \tag{A58}$$

It will be shown later that an analytical solution is available for equation A58.

$$\frac{dh(s)^{**}}{dt} = 2\beta w(s,s+1) + \delta v(s,s) + 2\sum_{i=1}^{s} h(i)^*w(s-i,s-i+1) + \sum_{i=1}^{s-1} h(i)^{**}v(s-i,s-i) - h(s)^{**}\left[\alpha + 2(\mu-1)X_1\right] \tag{A59}$$

$$\frac{dH^{**}}{dt} = 2\beta\left[W^* - w_1\right] + \delta V + 2H^*W^* + H^{**}V^* - H^{**}\left[\alpha + 2(\mu-1)X_1\right] \tag{A60}$$

Similar substitutions into the differential form of equation A42 yields

$$dG^{**}/dt = 2w_1\left[G^* + 2(\mu-1)X_1\right] - G^{**}\left[\gamma - 2f + 2(\mu-1)X_1\right] \tag{A61}$$

Let

$$\theta(i) = \left[\cdots x_nCCX_1CCx_m\cdots\right] \qquad n,\ m \neq 0,1$$

then

$$d\theta(s)/dt = \beta h(s)^{**} + \delta h(s)^* + \sum_{i=1}^{s-1} h(i)^*h(s-i)^{**} \tag{A62}$$

$$d\theta/dt = d\Sigma\theta(s)/dt = \beta H^{**} + \delta H^* + H^*H^{**} \tag{A63}$$

Substitution of the various equations into the differential form of equation A27 then summing over s yields

$$d\Sigma g(s)^{I}/dt = -G^{**}\left[G^* + 2(\mu-1)X_1\right] \tag{A64}$$

Equations A61 and A64 have not yet been solved analytically. The set of equations A58, A61 and A64 are simultaneous linear differential equations which can be solved numerically. Because equation A35 is difficult to evaluate numerically, it is easier to include the differential form, equation A34, in the list of simultaneous linear differential equations that need to be solved.

To eliminate time as a variable, which approaches infinity as the reaction goes to completion, divide each equation by equation A29.

It is now possible to find the number average number of X_1 units in a sequence, $X_1^c / \Sigma g(s)^I$. Also one can find the corresponding values of U^*, V^*, and W^*, that is, the concentration of isolated hard blocks from the simultaneous differential equations A48, A51 and A55.

The concentration of terminal sequences

$$H^* = G^* - V^* - 2U^* \tag{A65}$$

$$H^{**} = G^{**} - V^* - 2W^* + 2w_1 \tag{A66}$$

can also be determined. At complete reaction under stoichiometric conditions or with excess CC $U^* = V^* = W^* = H^* = 0$.

By including segment type 3 of Table 2 in the definition of a hard block segment, equation 27 must be modified

$$g(1)^{II} = \left[\cdots x_nCCx_m\cdots\right] + \left[\cdots x_nCC\right] + \left[X_1\right] + \left[v(1,1)\right] + \left[w(1,2)\right], \quad n,\ m \neq 0,1 \tag{A67}$$

$$g(s)^{II} = \left[\cdots x_nCC(X_1CC)_{s-1}x_m\cdots\right] + \left[\cdots x_nCC(X_1CC)_{s-1}\right] + \left[\cdots x_n(CCX_1)_s\right] + \left[u(s,s-1)\right] + \left[v(s,s)\right] + \left[w(s,s+1)\right], \quad n,\ m \neq 0,1 \qquad s \geq 2 \tag{A68}$$

and

$$\sum_{s=1}^{\infty} g(s)^{II} = \sum_{t=1}^{\infty} g(t)^{I} + \left[\cdots x_nCCx_m\cdots\right] + \left[\cdots x_nCC\right] \tag{A69}$$

$$d\Sigma g(s)^{II}/dt = d\Sigma g(s)^{I}/dt + \beta\delta + d\delta/dt \tag{A70}$$

Simplification of the above equation with the aid of equations A29, A53, and A58 gives

$$d(\Sigma g(s)^{II} - G^*)/d\gamma = -\gamma/2C_1 \tag{A71}$$

Under the boundary conditions $\Sigma g(s)^{II} = G^*/2 = X_1^o$ at $t=0$ and equation A53 one obtains

$$\Sigma g(s)^{II} = C_1 - X_1^o + G^* - w_1 \tag{A72}$$

The total number of AA units in hard block segments is given by

$$\Sigma sg(s)^{II} = A_1 - B_1 - \gamma + 2f + G^* \tag{A73}$$

hence $\bar{s}$ is equal to equation A73 divided by equation A72.

Under stoichiometric conditions at complete reaction

$$\bar{s} = C_1/(C_1 - X_1^o), \quad (A_1 = B_1 + C_1,\ t = \infty) \tag{A74}$$

For Model III, define

$$g(s)^{III} = \left[\cdots(xCC)_sx\cdots\right] + \left[\cdots(xCC)_s\right] + \left[\cdots(xCC)_sx\right] + \left[x(CCx)_s\right] + \left[(xCC)_s\right] + \left[CC(xCC)_{s-1}\right] \tag{A75}$$

where x represents either the terminal AA unit of an x_n sequence or an X_1 unit

then

$$d\Sigma g(s)^{III}/dt = d(\Sigma g(s)^{I} + \delta + w - X_1)/dt + \beta\delta = -\gamma(G^* - 2X_1) \tag{A76}$$

Combination of equations A76, A34, and A58 gives

$$d(\Sigma g(s)^{III} - G^*)/dt = 2\mu X_1\gamma = -dX_1/dt \tag{A77}$$

so

$$\Sigma g(s)^{III} - G^* = -X_1 + \text{constant} \tag{A78}$$

and from the boundary conditions.

$$\Sigma g(s)^{III} = C_1 - X_1^o + G^* - X_1 \tag{A79}$$

Again, at complete reaction under stoichiometric conditions equation A74 results.

Because X_1 is no longer considered to be an active group, we can write

$$G^{*III} = G^* - 2X_1 \tag{A80}$$

the differential form of A80, after substitution of equations A58 and A34 can be integrated to give

$$G^{*III} = \left[-X_1 + X_1^o(X_1/X_1^o)^{1/2\mu}\right]/\left[1 - 1/2\mu\right] \tag{A81}$$

so $\Sigma g(s)^{II}$ and $\Sigma g(s)^{III}$ can both be found without recourse to computer solutions.

To find the value of $\bar{s}$ when $\mu=\infty$ under stoichiometric conditions first let $X_1 \to 0$ to obtain equation A74, then evaluate X_1^o from equation A35 by allowing $\mu \to \infty$ to obtain

$$X_1^o = A_1 - 2B_1 \qquad (\text{when } \mu = \infty) \tag{A82}$$

which yields

$$\bar{s} = (A_1 - B_1)/B_1 \tag{A83}$$

APPENDIX B

THE NONSYMMETRICAL CASE

<u>The initial reaction rate constants of the monomer are different.</u>

The reaction of the nonsymmetrical molecule °AA' where the °-end of the molecule reacts with a rate constant k and the '-end reacts with a rate constant k', k and k' being independent of whether or not the other end has reacted. With essentially the same nomenclature used in describing the reaction of excess AA with BB, we can write $x_n^°$, x_n', x_n'', $y_n^°$, and y_n' where $x_n^°$ refers to molecules with °-type ends, x_n' refers to molecules with one °-type and one '-type end, x_n'' refers to molecules with two '-type ends, $y_n^°$ and y_n' referring to molecules with one B-type end and either a °- or a '-type end. In this case we must specify the total concentration of °- and '-type ends as

$$\rho = 2\sum_{n=2}^{\infty} x_n^° + \sum_{n=1}^{\infty} x_n' + \sum_{n=1}^{\infty} y_n^° \tag{B1}$$

$$\sigma = 2\sum_{n=2}^{\infty} x_n'' + \sum_{n=1}^{\infty} x_n' + \sum_{n=1}^{\infty} y_n' \tag{B2}$$

and the concentration of B-type ends is

$$Q = 2\sum_{n=0}^{\infty} z_n + \sum_{n=1}^{\infty} y_n^° + \sum_{n=1}^{\infty} y_n' \tag{B3}$$

The same restrictions are placed on $\mu = k'/k$ and $t = \int_0^{\tau} k\,d\tau$ as before.

We find

$$d\rho/dt = -\rho Q \tag{B4}$$

$$d\sigma/dt = -\mu\sigma Q \tag{B5}$$

hence
$$\sigma = \sigma_o(\rho/\rho_o)^{\mu} = A_1(\rho/A_1)^{\mu} \tag{B6}$$

The mass balance restriction requires

$$\rho + \sigma = Q + 2f' \tag{B7}$$

Hence the values of ρ_f and σ_f at complete reaction when Q = 0, can be determined. Furthermore the concentration of unreacted °AA' is

$$X_1^o = (X_1')_o = \rho_f\sigma_f/A_1 \tag{B8}$$

On addition of CC, the differential equations required for determining $\Sigma g'(s)^I$, the total concentration of hard block segments for the nonsymmetrical case, Model I, are

$$d\Sigma g'(s)^{I}/dt = -G^{**}(G^{°*} + \mu G'^*) \tag{B9}$$

$$dG^{**}/dt = 2w_1(G^{°*} + \mu G'^*) - G^{**}(\alpha^° + \mu\alpha') \tag{B10}$$

$$dG^{°*}/dt = -G^{°*}\gamma \tag{B11}$$

$$dG'^*/dt = -\mu G'^*\gamma \tag{B12}$$

where $G^{°*}$, G'^* are the corresponding values of G^* for active chains terminating in a °- or '-type end

$$Y = 2W^* + V^{\circ *} + V'^* \qquad \text{B13}$$

$$\alpha^\circ = 2U^{\circ *} + U'^* + V^{\circ *} \qquad \text{B14}$$

$$\alpha' = 2U''^* + U'^* + V'^* = \alpha'_e(\alpha^\circ/\alpha^\circ_o)^\mu = \sigma_f(\alpha^\circ/\sigma_f)^\mu \qquad \text{B15}$$

$$w_1 = (\alpha^\circ + \alpha' - 2f)^2/4C_1 \qquad \text{B16}$$

and f arises from the mass balance restriction

$$\alpha^\circ + \alpha' - 2f = Y \qquad \text{B17}$$

$$\rho_f + \sigma_f - 2f = 2C_1 \qquad \text{B18}$$

To eliminate time as a variable, each differential equation is divided by

$$d\alpha^\circ/dt = -\alpha^\circ Y \qquad \text{B19}$$

The above equations were obtained by the same procedures used in Appendix A.

The formulas for number average molecular weight and the number of monomers per polymer molecule are identical to those given earlier.

By including segment type 3 of Table 2 in the definition of a hard block segment, $d\Sigma g(s)^{II}/d$ can be integrated to give

$$\Sigma g(s)^{II} = C_1 - X_1^\circ + G^{\circ *} + G'^* - w_1 \qquad \text{B20}$$

where

$$G^{\circ *} = \sigma_f\alpha^\circ/A_1 , \quad G'^* = \frac{\rho_f\sigma_f}{A_1}\left[\frac{\alpha^\circ}{\sigma_f}\right]^\mu \qquad \text{B21}$$

The total number of AA units in hard block segments at any time t is similar to equation A73 with G^* replaced by $G^{\circ *} + G'^*$. At complete reaction under stoichiometric conditions, equation A74 is again obtained for $\bar{s}$. A similar result is

obtained for Model III. The total concentration of hard block segments for Model III is

$$\Sigma g(s)^{III} = C_1 - X_1^\circ + G^{\circ *} + G'^* - X_1 \qquad \text{B22}$$

APPENDIX C

The Statistical Model:

Case has considered the problem of molecule AA' reacting with BB where the reactivity of A differs from that of A' where a, a' and b are the fraction of reacted A, A' and B, respectively. (8) The conservation condition is

$$A_1(a + a') = 2bB_1 \qquad \text{C1}$$

and with the definitions

$$\eta = 2ab/(a + a') \qquad \text{C2}$$

$$\phi = 1 - 2b + 2b/(a - a') \qquad \text{C3}$$

The mole fraction distribution is

$$\begin{aligned} F(r) = {} & (1-b)^2(b\eta)^{r-1}/\phi \text{ for rBB units, r-1 AA' units} \\ & + 2b(1-b)(1-\eta)(b\eta)^{r-1}/\phi \text{ for rBB units, r AA' units} \\ & + (1-\eta)^2b^2(b\eta)^{r-1}/\phi \text{ for rBB units, r+1 AA' units, } r \geq 1 \\ & + 2(1-a)(1-a')/(a+a')\phi \text{ for unreacted AA' units} \end{aligned} \qquad \text{C4}$$

When b=1, the first two terms are zero, yielding a term for molecules with unspecified A-type ends and a term

equivalent to X_1°. Substitution of $a = 1 - \rho_f/A_1$ and $a' = 1 - \sigma_f/A_1$ into the last term yields equation 50 after conversion from mole fraction to concentration.

Case (9) also derived equations describing the distribution of a monomer AB polymerized to an extent of reaction a, then coupled with CC. However, his equations specify that the number of extender molecules per chain must be less than or equal to the number of AB molecules per chain. This restriction excludes molecules of the type W(s,s+1), hence cannot be used to calculate the number average number of AB molecules per hard block segment.

If the reactivity of the two ends of a diisocyanate monomer molecule are equal (μ=1), then the distribution of diisocyanate molecules per hard block segment can be calculated on the basis of statistical arguments. At the end of the reaction of AA with BB, $A_1 - B_1$ moles/ℓ remain, of which X_1° is unreacted AA. The mole fraction distribution can be obtained from the most probable distribution for AA reacting with BB taken from Case (8) or Flory (10), and setting b=1. The conservation condition requires that $a = B_1/A_1 < 1$ hence

$$F(r) = (1-a)a^r \qquad 0 \le r \le \infty \qquad \text{C5}$$

where r is the number of BB monomers per molecule. The concentration of unreacted AA is $F(0)(A_1 - B_1)$ which is

equation A22. Consider now any given C-end which is added as an extender. The probability of reacting with a monomeric A depends only on the ratio $X_1^\circ/(A_1-B_1)$ which will be called p. The probability of finding a sequence of s AA units in a hard block chain is just

$$P = p^s(1-p) \qquad \text{C6}$$

because the s+1 unit is a prepolymer chain which breaks the sequence. The normalized function is again the most probable distribution

$$F(r) = p^{s-1}(1-p) \qquad 1 \le r \le \infty \qquad \text{C7}$$

and the number average number of AA units per hard block segment is

$$\bar{s} = 1/(1-p) = A_1/B_1 \qquad \text{C8}$$

This is equation A74 where X_1° is given by equation A22.

APPENDIX D

Formulas for Single Stage Polymerization when μ = 1, Symmetrical Case

Model I is rather complex because the B-type end can compete with the C-type end. Further, an $h(1)^*$ by reaction with a B-type end becomes a soft segment. The formulas are

$$d\Sigma g(s)^I/dt = -G^{**}[G^* + 2(\mu - 1)u_1] - b[2\mu u_1 + h(1)^* + y_1] \qquad \text{D1}$$

$$dG^*/dt = -[G^* + 2(\mu - 1)u_1]Y - 2\mu b u_1 \qquad \text{D2}$$

$$dG^{**}/dt = 2w_1[G^* + 2(\mu - 1)u_1] - G^{**}[Y - 2f + 2(\mu-1)u_1] - by_1 \qquad \text{D3}$$

$$du_1/dt = -2\mu u_1 Y \qquad \text{D4}$$

$$dh(1)^*/dt = 2bu_2 + (Y - 2f - G^*)y_1 + 2(c - G^{**} - 2w_1)Yw_1 - h(1)^* \qquad \text{D5}$$

$$dy_1/dt = 4\mu w_1 u_1 - 2y_1[Y - f + (\mu-1)u_1] \qquad \text{D6}$$

$$du_2/dt = 2bu_1y_1 - 2u_2Y \qquad \text{D7}$$

$$c = KY = [C_1/(B_1 + C_1)]Y \qquad \text{D8}$$

$$b = (1 - K)Y \qquad \text{D9}$$

$$dY/dt = -[Y - 2f + 2(\mu - 1)u_1]Y \qquad \text{D10}$$

where u_1 = unreacted diisocyanate monomer; Y is the total concentration of hydroxyl groups, and is equal to b + c; b, c are the total concentration of B-type and C-type ends, respectively; y_1 = [AACC]; u_2 = [AACCAA]; and $h(1)^*$ = [BAACCAA]

When the extender is considered to be the active portion of the hard block, Model III, then the equation can be integrated

$$\Sigma g(s)^{III} = KG^* - K(2 - K)u_1 + C_1 - K^2A_1 \qquad \text{D11}$$

u_1 is a positive root of

$$2(\mu-1)Y/2A_1 = (\mu-1)(u_1/A_1) - (2\mu-1)f''/A_1 + (u_1/A_1)^{1/2\mu} \qquad \text{D12}$$

$$\text{where } f'' = B_1 + C_1 - A_1 \qquad \text{D13}$$

When $t = \infty$ and $Y = u_1 = f'' = 0$

$$\bar{s} = A_1/B_1 \quad (A_1 = B_1 + C_1,\ t = \infty) \qquad \text{D14}$$

which is independent of μ.

total concentration of internal segments is given by $\Sigma\theta(s)$ (see eq A62 and A63). Division of $\Sigma g(s)^I$ or $\Sigma\theta(s)$ by the concentration of polymer molecules yields the total and internal number of hard block segments per polymer molecule. For A_1 = 6 mol/l., only about 40% of the hard block segments are internal sequences at 95% conversion, the remaining 60% being terminal chains or isolated sequences. From 95 to 99% conversion, the per cent of internal sequences raises from 40 to 80%. Of course, at 100% conversion, all hard block segments are internal.

Conclusions

The sequence length distribution for the hard block segment in sequential block copolymers prepared by a two-stage process has been calculated from the derived kinetic expressions. Two cases are considered: one in which the diisocyanate monomer has a reactivity different from that of a terminal isocyanate group in a polymer chain, the other in which the reactivities of the isocyanate groups in the monomer differ because of steric reasons. Because there are no major differences in the results of the two cases, it is not considered worthwhile to extend the treatment by combining the two cases. A number of models of the hard blocks are considered wherein the method of counting the repeat unit is varied. All models considered lead to the same number average sequence length at 100% reaction under stoichiometric conditions. Such a result can only occur if the distribution of repeat units in the hard block segment is of the most probable form. The heterogeneity index of the hard block segments is less than 2 because only short sequence lengths are produced. Control of the sequence length and the molecular weight of the polymer can be affected by altering the proportions of diisocyanate, prepolymer, and extender and by the method of mixing the reactants.

Acknowledgments. I would like to thank Dr. N. S. Schneider, Army Materials and Mechanics Research Center, for suggesting the problem and Dr. Schneider and Mrs. Joyce Illinger for many stimulating discussions during the course of this work, in particular the suggestion that more than one model of the hard block segment should be considered. Professor J. J. Hermans, University of North Carolina, derived eq A21 in an unpublished work (1963) which formed the foundation for the present work. The arguments leading to its derivation in Appendix A are essentially those used by Professor Hermans. Permission to cite that work was granted by the Chemstrand Research Center, Inc. The cost for the computer calculations was supported by the Department of Chemical Engineering, MIT, and is greatly appreciated. I especially want to acknowledge the assistance of those mentioned above and the reviewers for helpful comments concerning the form of the manuscript.

Supplementary and Miniprint Material Available. The programs for computing $\Sigma g(s)$ for both the symmetrical and nonsymmetrical cases as a function of conversion will appear immediately following this article in the microfilm edition of this volume of the journal. Photocopies of the supplementary material and full-sized photocopies of the miniprint material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $6.00 for photocopy or $2.00 for microfiche, referring to code number MACRO-74-872.

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Thermodynamic Potential Functions for Elastomers

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Received May 23, 1974

ABSTRACT: The thermodynamic description of the large principal deformations of elastomers requires four thermodynamic energy functions and their associated free energies. The significance of, and relationship between, these potential functions is discussed and their interrelations are derived. The internal energy contribution to the retractive force or the extension in an elastomer is used as an example of the application of the concepts introduced.

The thermodynamic (more precisely thermostatic) description of the deformation of a solid system is more complex than that of a fluid (gas or liquid) system. In the latter, volume and pressure are the only mechanical parameters to be taken into account. In the former, the set of mechanical parameters must be enlarged, in the general case, to the 6 + 6 = 12 components of the strain and stress tensors.[1] This paper discusses the thermodynamic potential functions which are useful in describing the thermodynamics of large principal deformations of elastomers and the general relations between their differentials and those of various sets of independent variables. Because an elastomer may be regarded as a homogeneous isotropic solid, its deformation can be described more simply than that of a general solid. The potential functions for the thermodynamics of elastomers introduced here are defined in a way which makes them consistent with the definitions of the potential functions in the thermodynamics of fluids. The following discussion aims to provide an exhaustive treatment of the formalism of the thermodynamics of elastomers.

Potential Functions

The first law of thermodynamics gives the change in the internal energy U as

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W \tag{1}$$

where $\mathrm{d}Q$ is the element of heat absorbed, and $\mathrm{d}W$ is the element of work done, by the system on its surroundings. If the process is conducted reversibly

$$\mathrm{d}Q = T\mathrm{d}S \tag{2}$$

where T is the (absolute) temperature and S is the entropy. Flory[2] has shown that the element of elastic work, $\mathrm{d}W$, done by a homogeneous isotropic system in a large principal deformation is given by

$$\mathrm{d}W = -V\sum_{i=1}^{3} t_i \mathrm{d}\ln\lambda_i \tag{3}$$

where V is the deformed volume, the t_i are the principal true stresses, and the λ_i are the principal extension ratios defined as the ratios of the stretched lengths, L_i, to the unstretched lengths, L_{i0}.

Thus, the change in the internal energy is given by

$$\mathrm{d}U = T\mathrm{d}S + V\sum_i t_i \mathrm{d}\ln\lambda_i \tag{4}$$

and the change in the associated (Helmholtz) free energy, defined by

$$A = U - TS \tag{5}$$

becomes

$$\mathrm{d}A = -S\mathrm{d}T + V\sum_i t_i \mathrm{d}\ln\lambda_i \tag{6}$$

The last terms in eq 4 and 6 contain both the work of extension and the work of expansion. The two must be separated because changes in volume may be induced both by the application of forces or extensions and by changes in temperature. We consider that the principal true stresses are

$$t_i = (L_i f_i / V) - P \tag{7}$$