# Segmented Polyurethans. Properties as a Function of Segment Size and Distribution

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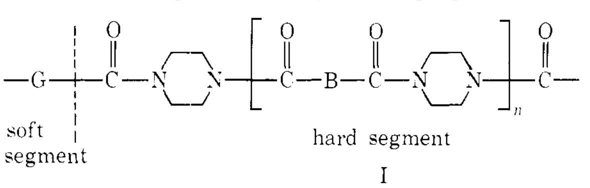
*Received June 27, 1969*

ABSTRACT: Property-structure relationships in a series of segmented polyurethans (I) have been studied. The structural features of interest—hard segment size, size distribution, and spacing along the chain (*i.e.*, soft segment distribution)—were varied independently by special synthetic techniques. The hard segments are crystalline and have well-defined melting points which increase with segment size. Reciprocal absolute melting temperature is inversely proportional to the number of repeat units in the segment. Degree of crystallinity varies little with size. Cocrystallization of different hard segments is a function of relative size. Narrowing of the hard segment size distribution increases modulus, tensile, and extension set drastically. Narrowing of the soft segment distribution causes a slight increase in modulus, a moderate increase in elongation and tensile, and a large increase in extension set.

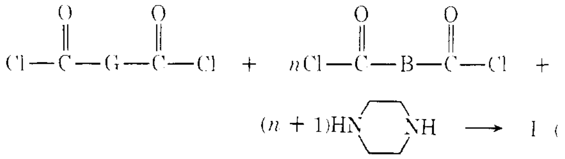
Segmented polyurethans represented by formula I are block copolymers composed of alternating soft and hard segments. They exhibit properties characteristic of cross-linked elastomers over a wide temperature range but, at higher temperatures, melt and can be processed by techniques used for plastics and fibers.[1] This behavior is explained by the fact that the polymers possess a three-dimensional network built up by intermolecular association (crystallization) of the hard segments. It was therefore of interest to study the effect upon polymer properties of changes in hard segment size, size distribution, and spacing along the polymer chain.



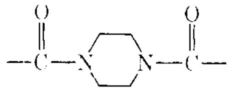
I

$G = \leftarrow OCH_2CH_2CH_2CH_2 \rightarrow_x O—$
$B = —OCH_2CH_2CH_2CH_2O—$

Polymers of formula I are most conveniently prepared by the chain extension of a mixture of chloroformates with piperazine in the presence of an acid acceptor. The structures of the resulting polymers are somewhat ill-defined, however, since the average size and size distribution of the hard segments are functions of *n*. A further complication arises from the fact that some of the soft segments are connected by the



$$Cl—\overset{O}{\overset{\|}{C}}—G—\overset{O}{\overset{\|}{C}}—Cl + nCl—\overset{O}{\overset{\|}{C}}—B—\overset{O}{\overset{\|}{C}}—Cl + (n+1)HN\langle\rangle NH \longrightarrow I \quad (1)$$



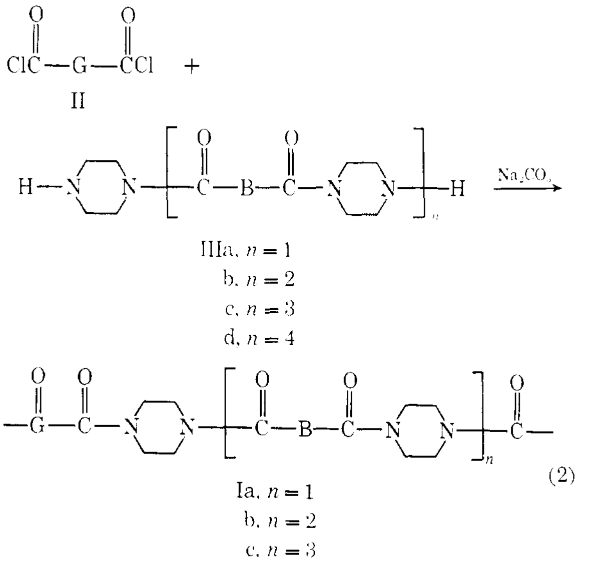
$$—\overset{O}{\overset{\|}{C}}—N\langle\rangle N—\overset{O}{\overset{\|}{C}}—$$

linkage which does not function as a hard segment and which serves only to alter the size distribution of the soft segments in the starting bischloroformate.

In order to separate the effects of the various structural features, it was decided to synthesize model polymers by special techniques which would permit independent control of each feature. The observed properties were then correlated with the features known to be present.

## Results and Discussions

**Preparation of Polymers with Monodisperse Hard Segment Size Distribution.** To satisfy the requirement that all hard segments within a given polymer be of the same size, it was decided first to synthesize the hard segments in a stepwise manner and then to introduce them into the polymer *via* a condensation reaction which would preclude the possibility of any changes occurring in segment size during the chain-extension step. The model polymers (Ia–d) were thus prepared by treating amine-terminated hard segments (IIIa–d) with polytetramethylene ether glycol bischloroformate (II) in the presence of an acid acceptor (eq 2).



$$Cl\overset{O}{\overset{\|}{C}}—G—\overset{O}{\overset{\|}{C}}Cl \quad (II) + H—N\langle\rangle N\left[—\overset{O}{\overset{\|}{C}}—B—\overset{O}{\overset{\|}{C}}—N\langle\rangle N—\right]_n H \xrightarrow{Na_2CO_3} —G—\overset{O}{\overset{\|}{C}}—N\langle\rangle N\left[—\overset{O}{\overset{\|}{C}}—B—\overset{O}{\overset{\|}{C}}—N\langle\rangle N—\right]_n \overset{O}{\overset{\|}{C}}— \quad (2)$$

II

IIIa, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$

Ia, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$

(2)

$G = \leftarrow O—CH_2CH_2CH_2CH_2 \rightarrow O_{13.7}—$

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(1) Manfred Katz, U. S. Patent 2,929,802 (1960).

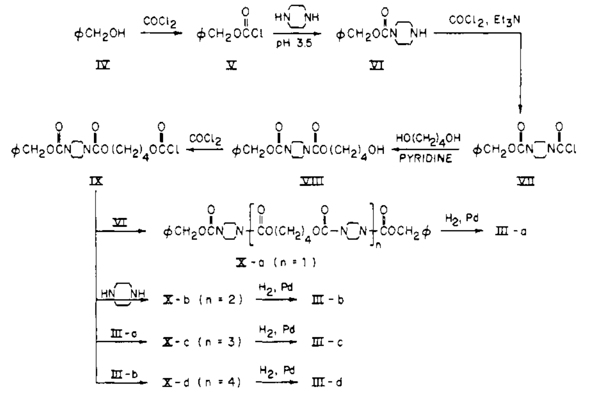

Figure 1. Synthesis of amine-terminated hard segments.

This reaction is fast, relatively free of side reactions, and produces high molecular weight polymers provided the reactants are bifunctional and the stoichiometry is properly balanced.[2]

Very high quality II is easily available from commercial polytetramethylene ether glycol (PTMEG) by treatment of the latter with excess phosgene. IIIa–d have not been prepared previously. The successful synthesis of these compounds in a high state of purity and with a high degree of bifunctionality therefore constituted the major obstacle to be overcome in the synthesis of the desired polymers.

IIIa–d were synthesized by the routes shown in Figure 1. The over-all synthesis depends upon the successful preparation of the key reagent IX. The latter is important because it contains one repeat unit of the hard segment, a chloroformate group which reacts readily and quantitatively with amine groups, and a carbobenzyloxy protective group on one of the nitrogen atoms which is easily and selectively removed by hydrogenolysis.[3]

Further extension of any member of the III series by two repeat units at a time is easily accomplished by reaction with an excess of IX followed by removal of the carbobenzyloxy protective groups. IIIa is the starting point for the series containing an odd number of repeat units, and IIIb the even number. IIIa is prepared by treating VI with IX and then removing the protective groups. IIIb is obtained by treating 2 mol of IX with piperazine followed by hydrogenolysis of the resulting product.

All of the intermediates were highly purified before being used in the next reaction except VIII and IX. The primary impurity in both of these compounds was Xa. Since it occurred in all reaction products prepared with IX, it was also an impurity in Xb, Xc, and Xd. Xa differed appreciably in solubility from the latter three compounds, however, and was easily removed during the recrystallization of these compounds.

Some difficulty was encountered in the purification of the higher members of the III series. As the number of repeat units increased, the solubility in water-immiscible solvents became quite limited except in chlorinated solvents such as methylene chloride, chloroform, and 1,1,2-trichloroethylene. These solvents were satisfactory for water extractions that were needed to remove acids, bases, and inorganic salts from the reaction products, but they did cause complications because of chemical reactions which sometimes occurred between the chlorinated solvent and the amine groups of the reaction product. In such cases it was observed that the amine titer of the product decreased, and chlorine was found in the reaction product. The side reaction involved is probably an alkylation of the amine groups by the chlorinated solvent which has been reported by other workers.[4] It is free radical in nature and is catalyzed by trace quantities of heavy metals. In all cases where it was necessary to handle an amine-containing compound in the presence of a chlorinated solvent, the contact time between the two was kept at an absolute minimum.

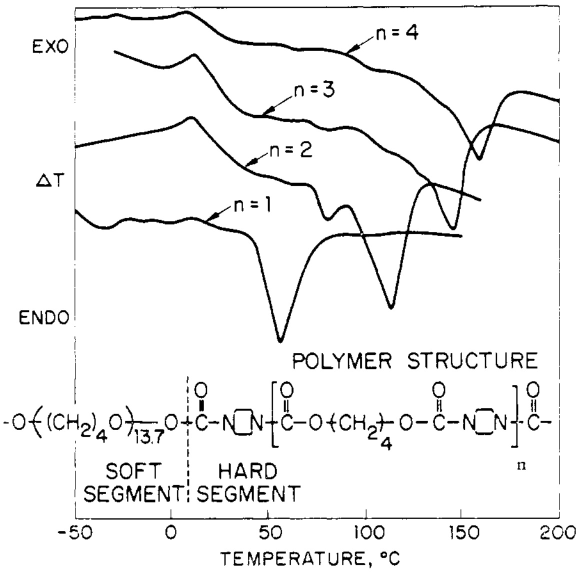

Figure 2. Differential calorimetric scans of polymers with monodisperse hard segment sizes.

The amine-terminated hard segments had elemental analyses quite close to the calculated values and amine titers between 98.1 and 100% of the theoretical value. They were also essentially bifunctional as indicated by the fact that the polymers prepared from them (Table I) had high inherent viscosity values.

Table I
Properties of Segmented Polyurethans with Monodisperse Hard Segment Distributions

| Polymer | % N Found | % N Calcd | Inherent viscosity[a] |
|---|---|---|---|
| Ia | 4.09 | 4.09 | 2.52 |
| Ib | 5.26 | 5.18 | 2.61 |
| Ic | 6.07 | 6.08 | 2.59 |
| Id | 6.80 | 6.75 | 2.13 |

[a] *m*-Cresol, 0.1%, 30°.

**Effect of Hard Segment Size upon Thermal Stability of Polymer Network.** Thermal stability of the polymer

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(2) P. W. Morgan, "Condensation Polymers," Interscience Publishers, New York, N. Y., 1965.

(3) W. H. Wartung and R. Simonoff, *Org. Reactions*, 7, 263 (1953).

(4) W. C. Davies, E. B. Evans, and F. L. Hulbert, *J. Chem. Soc.*, 412 (1939); N. H. Cromwell, P. W. Foster, and M. M. Wheeler, *Chem. Ind.* (London), 228 (1959).

networks in Ia–d were investigated by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). DSC scans are shown in Figure 2. The hard segments exhibit sharp, endothermic, fusion peaks. Segment melting point increases with the number of repeat units in the segment and approaches asymptotically the melting point of the homopolymer of the same composition as the hard segment repeat unit.

Flory[5] has derived eq 3 to describe the melting points of homopolymers of different degrees of polymerization where $T_m$ is the melting point, $R$ the gas constant, $n$ the number of repeat units, $\bar{H}_n$ the average heat of fusion per repeat unit, and $T_m{}^\circ$ the melting point of the infinite polymer. This equation is based

$$\frac{1}{T_m} = \frac{2R}{n\bar{H}_n} + \frac{1}{T_m{}^\circ} \qquad (3)$$

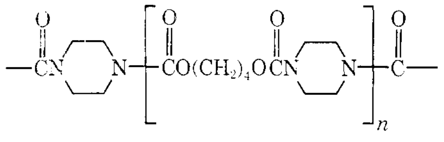
on the assumption that chain ends function as diluents and thus serve to lower the melting point depending upon their concentration. The same arguments could also be applied to the hard segments in the segmented polyurethans if the hard and soft segments were not miscible. It has not been firmly established that this condition exists although it has been observed that the melting point of a given hard segment does not change appreciably as the hard segment concentration changes. An excellent correlation of melting point *vs.* hard segment size is obtained, however, by plotting reciprocal absolute melting temperature *vs.* the reciprocal of the number of repeat units in the hard segment as shown in Figure 3.

Heats of fusion of the model polymers (IIIa–d) were determined from the areas of the fusion peaks in the DSC scans. These values could then be related to the hard segment since composition of each polymer was accurately known. The experimental heats of fusion (Table II) are quite similar. This indicates that fractional crystallinity of the hard segments varies little with size.

TABLE II
HEATS OF FUSION OF HARD SEGMENTS OF DIFFERENT LENGTHS

| No. of repeat units in hard segment | Hard segment, wt, %[a] | $\Delta H_f$, cal/g Polymer | Hard segment |
|---|---|---|---|
| 1 | 27.2 | 2.7 | 9.9 |
| 2 | 37.6 | 3.2 | 8.5 |
| 3 | 46.0 | 4.4 | 9.6 |
| 4 | 51.6 | 5.0 | 9.7 |
| Homopolymer | 100 | 11.4 | 11.4 |

[a] Based on the unit



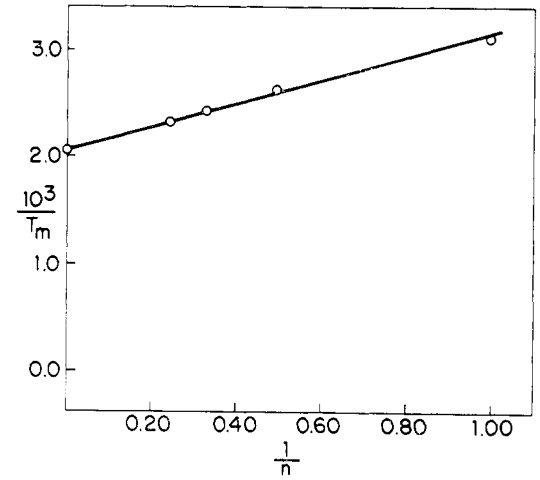


Figure 3. $1/T_m$ *vs.* $1/n$ for hard segments of different lengths.

**Melting Behavior of Mixtures of Different Hard Segments.** Since the segmented polyurethans I made under practical conditions (eq 1) contain hard segments of many different lengths,[6] it was of interest to study the interaction of hard segments of different size and to determine whether or not cocrystallization occurs.

Various combinations of the model polymers (Ia–d) containing equimolar quantities of the different size segments were examined. The mixtures were prepared by dissolving the polymers in chloroform and casting films.

Some combinations produced clear, transparent films similar to those obtained from the individual polymers while others produced white, opaque ones.

DSC traces of the opaque films are shown in Figure 4. Fusion peaks of the individual hard segments are present in these mixtures, but no new ones are evident.

Traces of the clear films all showed new fusion peaks as illustrated in Figure 5. A summary of fusion

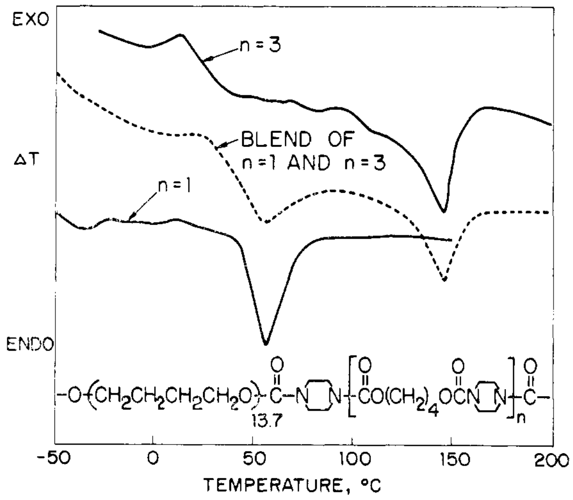


Figure 4. DSC scans of individual polymers and physical blend (opaque).

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[5] P. J. Flory, *J. Chem. Phys.*, **15**, 684 (1947); P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 570.

[6] L. E. Nielsen, "Mechanical Properties of Polymers," Reinhold Publishing Corp., New York, N. Y., 1962, p 25.

Table III
Fusion Peaks of Polymer Blends Containing Hard Segments of Various Sizes

| Model polymer blend composn[a] | Fusion peaks characteristic of individual hard segments, °C 1 | 2 | 3 | 4 | New fusion peaks, °C | | | |
|---|---|---|---|---|---|---|---|---|
| 1 and 2 | 54 | 112 | | | 0 | 90 | | |
| 1 and 3 | 54 | | 146 | | | | | |
| 1 and 4 | 55 | | | 160 | | | | |
| 2 and 3 | | 112 | 144 | | | 64 | 102 | |
| 2 and 4 | | 112 | | 160 | | 63 | | 147 |
| 3 and 4 | | | 146 | | | | 107 | 151 |

[a] Numbers refer to number of repeat units in individual hard segments. Blends contain equimolar quantities of each hard segment.

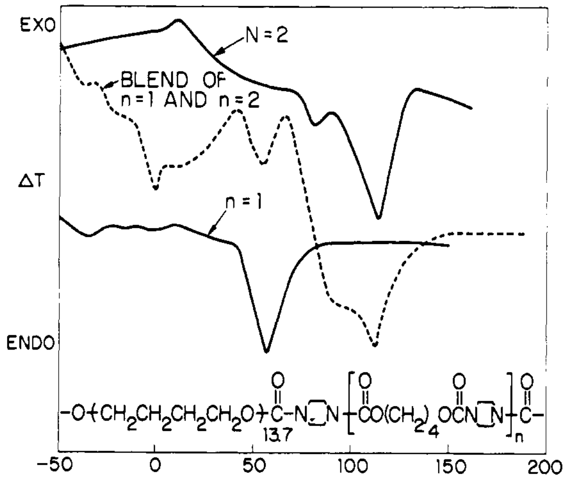

Figure 5. DSC scans of individual polymers and physical blend (transparent).

peaks for the various combinations is given in Table III. All of the clear films had peaks characteristic of the two individual hard segments present and, in addition, at least two new peaks. The latter are considered to be depressed melting points indicative of cocrystallization. It is significant that the hard segment with one repeat unit cocrystallizes with a segment containing two units but not with segments containing three or four units. Whether or not this behavior would apply to combinations of segments containing two, three, or four units with a second very long hard segment is not known.

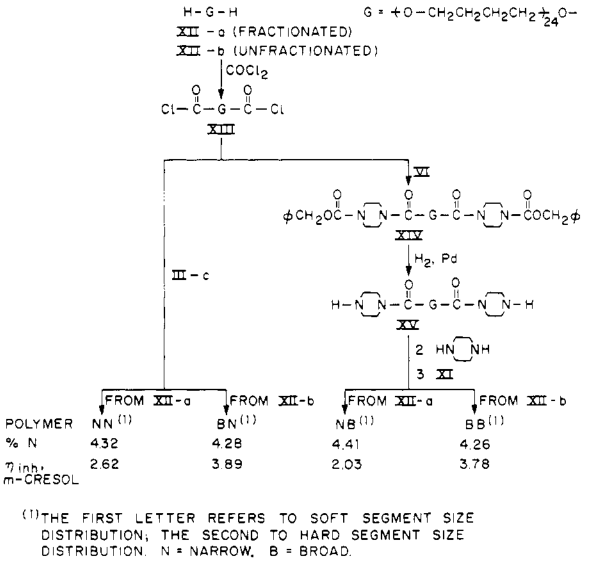

Figure 6. Preparation of polymers with different segment size distributions.

**Preparation of Polymers with Variations in Segment Size Distribution.** In order to study the effects of segment size distribution, a series of polymers with the same gross composition but with independent variations in size distribution of the two different segments was synthesized as shown in Figure 6.

A sample of PTMEG was converted into a bischloroformate by treatment with phosgene. One-half of this glycol was then treated with amine-terminated, performed hard segment to produce a polymer with a monodisperse hard segment size distribution which was representative in this series of a narrow distribution. A polymer with the same soft segment size distribution but with broader hard segment size distribution was prepared by treating the other half of the bischloroformate with carbobenzyloxypiperazine[7] (VI). This reaction served the purpose of capping the glycol and preserving the molecular weight distribution of the polytetramethylene ether units present in the original glycol. After removing the carbobenzyloxy protective groups by hydrogenolysis, the amine-terminated derivative of the starting glycol was mixed with piperazine, and the mixture was chain-extended with 1,4-butanediol bischloroformate (XI). Since the two different amines are in competition for the bischloroformate in the latter reaction, the sizes of individual hard segments are statistically determined,[6] and the size distribution is broad compared to that of the first polymer.

In the above reaction sequences, the size distribution of the polytetramethylene ether segments in the polymer is the same as in the starting glycol. Thus, soft segment size distribution can be conveniently varied by proper choice of the molecular weight distribution of the PTMEG. A sample of commercial PTMEG which was known to have a broad molecular weight distribution was used for preparation of model polymers containing broad soft segment size distributions. Polymers with narrower distributions were obtained by using a fractionated sample of PTMEG of the same number average molecular weight as above.

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(7) L. Goldman and J. H. Williams, *J. Org. Chem.*, **18**, 815 (1953); L. Goldman, U. S. Patent 2,617,804 (1952).

**Effect of Segment Size Distribution upon Polymer Properties.** Properties of the four model polymers containing various combinations of broad and narrow distributions of the two types of segments are shown in Figure 6. Gross compositions are similar as indicated by nitrogen content. Inherent viscosities are not the same but are nevertheless high enough that the differences did not affect the polymer properties investigated.

Stress–strain properties of these polymers are shown in Figure 7. It is obvious that hard segment size distribution has a profound effect upon stress at a given strain since the narrow distribution produces a much higher value than that of the broad distribution.

The main effect of soft segment size distribution is upon elongation and tensile strength with the narrow distribution producing the greater values of each.

Figure 8 shows the effect of size distribution upon extension set properties. The highest sets are produced where both segments have narrow distributions and the lowest where both segments have broad distributions.

## Experimental Section

**Preparation of Ia–d.** A solution of II (13.356 g, 0.012 mol) in $CH_2Cl_2$ was mixed in a 1-qt Osterizer blender with a $CH_2Cl_2$ solution of amine-terminated hard segment (IIIa,b,c, or d, 0.012 mol), the total quantity of $CH_2Cl_2$ used being equivalent to 10 ml/gram of calculated polymer yield. An aqueous solution of $Na_2CO_3$ (10%, 0.0288 mol, 3.053 g) was then added, and the mixture stirred vigorously for 10 min. The polymer was isolated in the blender by removal of the $CH_2Cl_2$ with steam, washed free of salts with hot water, and dried in a vacuum oven with a $N_2$ purge at 40–70°. Properties of the polymers are given in Table I.

**Preparation of II, XIIIa, and XIIIb.** These bischloroformates were prepared by adding the sample of PTMEG dropwise with agitation at 8–15° to liquid $COCl_2$ (10 mol/mole of hydroxyl), the reaction being carried out in the apparatus described for the preparation of V. After the addition was complete, the mixture was stirred for 2 hr during which time the temperature was allowed to rise to 25°. HCl and excess $COCl_2$ were removed by sparging the reaction mixture with $N_2$ *in vacuo*. The bischloroformates were stored at 0° until used.

**Preparation of IIIa, b, c, and d.** Starting material (Xa, b, c, or d, 30 g) was dissolved in glacial acetic acid at 50–60°. Catalyst (5% palladium on activated charcoal, Chemetron Chemicals, 3.0 g) was added, and the mixture treated with $H_2$ in a Parr hydrogenation apparatus for 2 hr at an initial pressure of 55 psig. Catalyst was removed by filtration, and most of the acetic acid by evaporation *in vacuo* in a rotary evaporator. The residue was dissolved in $H_2O$, the pH adjusted to >13 with KOH solution, and the product extracted with $CH_2Cl_2$. The extract was dried over $Na_2SO_4$ and then evaporated to dryness. The crude products were purified by recrystallization from appropriate solvents.

Recrystallization of IIIa from heptane produced white needles (92% yield), mp 97–98°, 100% purity by amine titration. *Anal.* Calcd for $C_{14}H_{26}N_4O_4$: C, 53.5; H, 8.34; N, 17.8. Found: C, 53.8; H, 8.35; N, 17.7.

Recrystallization of IIIb from a 1/3 v/v mixture of heptane and benzene produced a white crystalline solid (88% yield), mp 126.5, 99.1% purity by amine titration. *Anal.* Calcd for $C_{24}H_{42}N_6O_5$: C, 53.1; H, 8.0; N, 15.5. Found: C, 53.4; H, 8.0; N, 15.3.

Recrystallization of IIIc from a 1/8.3 v/v water–tetrahydrofuran mixture produced a white powdery solid (88.8% yield), mp 147–148°, 98.1% purity by amine titration. *Anal.* Calcd for $C_{34}H_{58}N_8O_{12}$: C, 53.0; H, 7.6; N, 14.5. Found: C, 53.1; H, 7.6; N, 14.6.

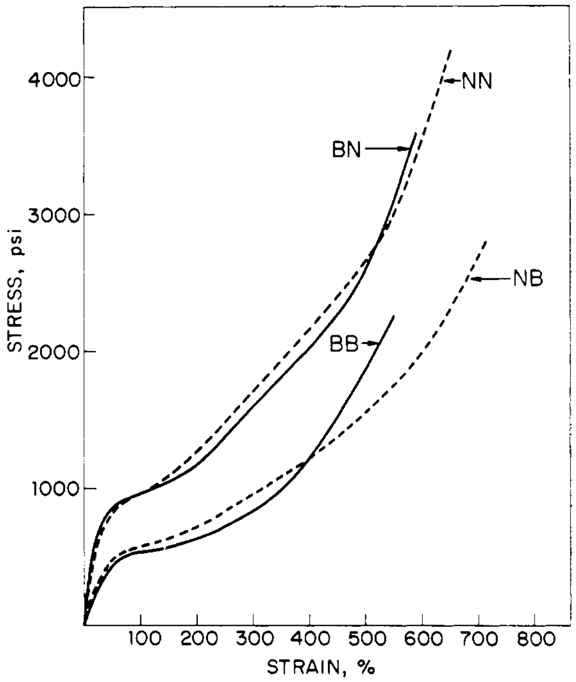

Figure 7. Stress–strain properties as a function of segment size distribution.

Crude IIId (98.4% yield) was recrystallized from a 1/9 water–tetrahydrofuran mixture. The resulting solid was dried, dissolved in $CH_2Cl_2$, the solution filtered, and the product precipitated with petroleum ether. The powdery white solid melted at 169° and was 98.75% pure by amine titration.

**Preparation of V.** Benzyl alcohol (13.5 mol, 1460 g) was added dropwise with good agitation to liquid phosgene (20.25 mol, 2001 g) over a period of 5 hr at 7–9.5°, the reaction being carried out in a 3-l. flask equipped with agitation, addition funnel, $N_2$ inlet tube, and reflux condenser which was cooled with acetone at −70° and which was connected in series to a drying tube, bubbler, and $NH_3$

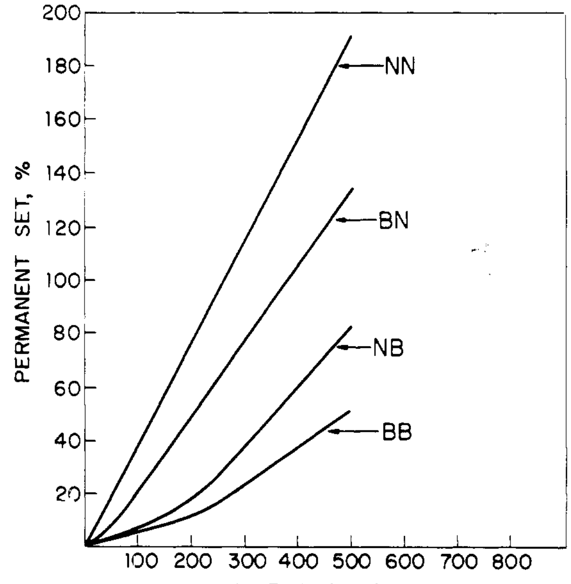

Figure 8. Extension set properties as a function of segment size distribution.

scrubber. The mixture was allowed to stand overnight in a Dry Ice/acetone bath after which HCl and excess phosgene were removed by sparging with $N_2$ *in vacuo*. The product weighed 2300 g and contained 20.3% active Cl (calcd for $C_8H_7ClO_2$, 20.8%).

**Preparation of VI.** VI was prepared by a previously reported procedure.[7] Purity was 98.2% by potentiometric titration.

**Preparation of VII.** A solution of VI (1.5 mol, 330.5 g), (triethylamine, 1.5 mol, 151.8 g), and dry ether (1800 ml) was added dropwise with good agitation at −65 to −60° over a 2-hr period to a solution of $COCl_2$ (7.5 mol, 742 g) in dry ether (450 ml). Stirring was continued for 0.5 hr after addition was complete. The mixture was filtered, the filter cake washed with dry ether (2000 ml), and the filtrate evaporated to dryness *in vacuo*. The crude product, a white crystalline solid, was obtained in 386.9 g (91.2% yield) and melted at 58.5–60°. *Anal.* Calcd for $C_{13}H_{15}ClN_2O_3$: C, 55.2; H, 5.4; Cl, 12.5; N, 9.91. Found: C, 55.3; H, 5.3; Cl, 12.6; N, 9.95.

**Preparation of VIII.** VII (0.1 mol, 28.27 g), 1,4-butanediol (0.6 mol, 54.07 g), and dry pyridine (50 ml) were heated at 137° for 1 hr. The reaction mixture was cooled, diluted with $H_2O$ (100 ml), and extracted three times with 100-ml portions of $CH_2Cl_2$. The extract was washed in succession with $H_2O$, 10% HCl, 5% $NaHCO_3$, and $H_2O$, dried over $Na_2SO_4$, filtered, and the solvent removed from the filtrate *in vacuo*. The crude product, a viscous liquid which slowly crystallized at room temperature, was obtained in 32.9 g (97.8%) yield. *Anal.* Calcd for $C_{17}H_{24}N_2O_5$: C, 60.7, H, 7.2; N, 8.33. Found: C, 59.6; H, 7.2; N, 7.88.

**Preparation of IX.** Crude VIII (0.5 mol, 168.2 g) in dry tetrahydrofuran (135 ml) was added dropwise with agitation to liquid $COCl_2$ (1.5 mol, 148 g) at 1–10° over a period of 75 min. Agitation was continued for 2 hr after the addition was complete. Solvent, HCl, and excess $COCl_2$ were removed by sparging with $N_2$ *in vacuo*. The crude product, a clear liquid, was obtained in 198.7 g (99.7%) yield and contained 8.44% active Cl (theory, 8.89%), indicating a purity of 95.0%.

**Preparation of Xa, b, c, and d.** These compounds were prepared by the following generalized procedure. Solid reactant (VI, 0.4 mol, piperazine, IIIa, or IIIb, 0.2 mol) was added with good agitation to a solution of crude IX (0.402 mol) in $CH_2Cl_2$ (1268 ml) in a Waring Blendor. A 10% solution of $Na_2CO_3$ (0.44 mol, 46.6 g) was added, and the emulsion stirred for 10 min. The two phases were separated, and the organic phase was washed with water and dried over $Na_2SO_4$. Evaporation of the solution produced a crude solid product which was purified by recrystallization. IIIa was recrystallized from ethanol; IIIb–d from a 3/1 v/v mixture of ethanol and chloroform.

IIIa was obtained in 98.4% yield and melted at 136.4–137°. *Anal.* Calcd for $C_{30}H_{38}N_4O_8$: C, 61.8; H, 6.6; N, 9.6. Found: C, 61.8; H, 6.5; N, 9.6.

IIIb was obtained in 86.6% yield and melted at 167–167.5°. *Anal.* Calcd for $C_{40}H_{54}N_6O_{12}$: C, 59.3; H, 6.7; N, 10.4. Found: C, 59.3; H, 6.7; N, 10.2.

IIIc was obtained in 91.3% yield and melted at 180–181°. *Anal.* Calcd for $C_{50}H_{70}N_8O_{16}$: C, 57.8; H, 6.8; N, 10.8. Found: C, 57.6, H, 6.8; N, 10.6.

IIId was obtained in 87.3% yield and melted at 184–186°. *Anal.* Calcd for $C_{60}H_{86}N_{10}O_{20}$: C, 56.9; H, 6.8; N, 11.0. Found: C, 56.9; H, 6.8; N, 10.9.

**Preparation of XIV.** XIIb (0.03 mol, 55.29 g), VI (0.066 mol, 14.54 g), and $CH_2Cl_2$ (400 ml) were mixed in a 1-qt Osterizer blender. A 10% solution of $Na_2CO_3$ (0.072 mol, 7.63 g) was added with vigorous agitation, and the mixture was stirred for 15 min. The mixture was diluted with $CH_2Cl_2$ (300 ml) and then washed in succession with $H_2O$, 5% HCl, and $H_2O$. After filtering, solvent and $H_2O$ were removed by heating *in vacuo* in a rotary evaporator. The product weighed 65.9 g (96.4% yield). *Anal.* Calcd for IV: C, 65.2; H, 10.0; N, 2.53. Found: C, 65.3; H, 10.0; N, 2.47.

**Preparation of XV.** IVb (0.0147 mol, 32.5 g), ethanol (190 ml), $H_2O$ (10 ml), concentrated HCl (3.0 ml), and catalyst (3.3 g, 5% Pd on activated charcoal, Chemetron Chemicals) were treated with $H_2$ in a Parr hydrogenation apparatus for 2 hr at an initial pressure of 55 psig. Catalyst was removed by filtration and most of the alcohol by evaporation *in vacuo* in a rotary evaporator. The residue was dissolved in benzene and washed with 10% NaOH and $H_2O$. The solution was dried over $Na_2SO_4$, filtered, and the filtrate evaporated *in vacuo* in a rotary evaporator. The product weighed 26.6 g (93.0% yield) and contained 1.024 mequiv of amine per gram (calcd 1.029).

**Preparation of Polymers NN and BN.** These polymers were prepared by a procedure similar to that described for Ia–d. Properties of the polymers are given in Figure 6.

**Preparation of Polymers NB and BB.** A solution of XV (0.015 mol, 29.15 g) and piperazine (0.0471 mol, 4.07 g) in $CH_2Cl_2$ (215 ml) was mixed with a solution of 1,4-butanediol bischloroformate (0.06 mol, 13.08 g) in $CH_2Cl_2$ (215 ml). A 10% solution of $Na_2CO_3$ (0.144 mol, 15.26 g) was added and the mixture stirred vigorously for 10 min. The polymer was isolated in the blender by flashing off the solvent with steam. The crumb was washed free of salts with hot water and dried in a vacuum oven at 70°. Properties of NB and BB are given in Figure 6.

**DTA and DSC Measurements.** These were made on an apparatus similar in design to the Du Pont Model 900 differential thermal analyzer. It was equipped with cells and the calorimetric attachment of the Model 900. Polymer samples consisted of porous crumbs. The reference was glass for DTA measurements and air for DSC measurements. The programmed heating rate was 12°/min.

**Test Specimens.** Stress-strain measurements were made on 0.25 × 5.0 × 0.020 in. strips died out from compression molded slabs (3.0 × 5.0 × 0.020 in.). The slabs were compression molded at a platten pressure of 40 *M* psi and at a temperature 25–30° above the melting point of the hard segments in the polymer. The samples were heated at these temperatures for approximately 5 min after which the press was cooled as rapidly as possible with cold water to 25°, the sample being maintained under pressure during the cooling cycle.

**Stress–Strain Measurements.** These were made on an Instron machine at a crosshead speed of 20 in./min.

**Extension Sets.** The specimen was pulled to the desired elongation at 20 in./min, removed from clamps, allowed to recover for 5 min, and the length measured.

**Fractionation of PTMEG.** A belt fractionator was used with solvent/nonsolvent mixtures composed of isopropyl alcohol and water. The original glycol ($\bar{N}_n$ = 1003) was separated into ten fractions, and the fraction with $\bar{N}_n$ = 1756 which represented 16.0% of the original PTMEG was used in preparing polymers NN and NB.

**Acknowledgments.** The author expresses his appreciation to W. P. Morgan for experimental assistance and to Drs. E. K. Gladding and R. Pariser for valuable discussions and encouragement.