

Biconstituent Fibers from Segmented Polyurethanes and Nylon 6

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Synopsis

The characteristics of Monvelle, a new biconstituent fiber from nylon 6 and a segmented polyurethane, are reviewed briefly, and some of the technical problems inherent in producing such a fiber are discussed. The characterization of two series of polyurethanes which can be melt spun is given in detail. The chemical composition of the hard segment was maintained constant, being derived from 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol, in all polymers. In one series using poly(butylene adipate) of MW 2000 as the soft segment, the average hard segment content was varied from 33% to 54%. In the other series, the hard segment content was held at 43%, and three additional soft segments, each at MW 2000, were used: poly(ethylene adipate), polycaprolactone and poly-1,4-oxybutylene glycol (PBG). Characterizations include molecular weight distributions, thermal analysis, rheological studies, and selected small-angle and wide-angle x-ray diffraction and polarized light microscopy. Crystallinity, melt viscosity, and activation energy of flow increased with increasing hard-segment content. Changes in the polyester soft segments had little effect on the properties studied, but with PBG the crystalline melting point of the polymer, without annealing, was higher and the melt viscosity was slightly higher than corresponding polyester-based samples, in agreement with previous reports of sharper phase separation in polyether urethanes, compared to polyester urethanes.

INTRODUCTION

The production of bicomponent fibers is well known, and several types have been commercially available for some time. Where the two components are in a side-by-side configuration, the first commercial materials were limited to those in which the components were closely related chemically ("bicomponent"), as in the cases where nylon 6 or 66 is conjugately spun with a nylon copolymer. Such fibers are self crimping because of the greater shrinkage of the copolymer, and they are of use in numerous textured yarn types. When the two components were not closely related chemically ("biconstituent" fibers), the commercially successful types were limited to sheath-core configurations, or those in which a minor component was distributed more or less uniformly as a second phase in the major component. Examples of the latter type are the antistatic nylons where a small percentage of a polyether is dispersed in the nylon melt prior to spinning.

In very recent years, the science and technology of melt spinning bicomponent systems have been extended to permit the commercial production of biconstituent fibers in side-by-side configuration from drastically different polymers. This

permits the production of fibers having properties which are quite different from those previously available.

At the Textile Research Institute meeting in April, 1973, Monsanto announced its new biconstituent fiber, Monvelle.¹ This fiber is a side-by-side conjugate with nylon 6 and a segmented polyurethane in a 50:50 volume ratio. This fiber is sold in the drawn state, in flat (uncrimped) form. It is thus readily knit into hosiery, and when the hose is immersed in hot water, a vigorous crimp develops. The resulting hose has excellent stretch characteristics, combined with power typical of support hose. The crimp development, stretch, and power characteristics result from the use of two such different polymers in the spinning.

When spun Monvelle fiber or yarn is drawn about $4\times$, the nylon component draws in the normal way, while the polyurethane stretches elastically. If the tension on the fiber is relaxed immediately after drawing, the fiber develops a tight, helical crimp.¹ When the fiber is wound on a bobbin immediately after drawing and stored at room temperature, the nylon portion cools below its glass transition temperature and stabilizes the structure. It is possible that the soft segments of the polyurethane crystallize in the extended state, based on x-ray studies of similar polymers by Bonart et al.² Then, if the fiber is removed from the bobbin, very little crimp is developed until it is heated above the nylon glass transition temperature and above the polyurethane soft-segment melting point. The best crimping is obtained upon immersing the fiber in water at 60°C or higher. The elastic recovery of the polyurethane then provides the necessary crimping force for texturing.

The conjugate spinning of two drastically different polymers such as nylon and an elastomer in side-by-side configuration has presented some very challenging technical problems. One of the first was associated with adhesion: many elastomers do not adhere adequately to conventional fibers such as nylon or polyester. While several combinations can be conjugately spun, the filaments usually split during drawing or, worse yet, during wear. When modifications are made to improve this adhesion, one usually gets the added result that the spun fiber sticks to itself on the bobbin and cannot be successfully drawn. Certain polyurethanes can be designed to overcome both problems, however, and permit spinning and drawing at commercial speeds.

Other problems arise in understanding and controlling the complex rheology of conjugate systems. The flow behavior must be balanced in a consistent way so that the same cross section is always obtained in the fiber, if one is to have uniform crimping performance and associated physical properties. When the two components accept dyes differently, uniformity of appearance requires very close control of the fiber cross-sectional structure, including the interface between the two components. Some of our fundamental studies on the rheology of conjugate flow have been published recently.³⁻⁵ Factors which are important in controlling interface shape include, first, a proper match of viscosities of the two polymers and, secondarily, polymer elasticity and interfacial tension effects.

Along with advances in polymer science, the engineering requirements of spinning nylon and an elastomer are formidable. These have led to extensive changes in the design of our spinning machines, which have contributed greatly to the success of this commercial operation.

Within the framework of this overview of the conjugate spinning of nylon and a polyurethane, let us now look more closely at some of the polymer characteristics

which are important for use in such a biconstituent fiber. Nylon 6 has been well characterized in the literature, and relatively little need be said about it here. The commercially successful melt spinning of polyurethanes is rare, if not unique, however, and considerably less has been published characterizing such materials. For this reason, the remainder of this paper will present a survey of properties of two series of model polyurethanes which can be melt spun. Additional details of these characterizations are planned for later publications.

Some of the general requirements for the polyurethane are that it be melt-spinnable at commercial speeds, have adequate thermal stability under spinning conditions, have good adhesion to the nylon yet not cause filaments to stick together on the bobbin, have adequate color and color stability for the intended applications, provide the retractive power needed for fiber crimping, and contribute suitably to overall fiber properties.

The requirements for melt spinning at commercial speeds and the necessary melt stability are rigorous. Problems with polymer reactions, including thermal decomposition at 200°C and above, are well known with polyurethanes. Thus, the problems due to limitations in thermal stability may place an upper limit on the spinning temperature. Certain other considerations, however, lead the polymer design chemist toward polyurethanes with as high a melting point as is practical. For best fiber properties, one wants an elastomeric component which will have little stress relaxation in the stretched state on the bobbin, will provide a strong elastic recovery force for crimp development, will have as low a hysteresis as possible in the crimped form, and will contribute significantly to the decrimping force required to stretch the final garment. The need for melt spinning further requires that these properties be obtained without chemical crosslinking. At this time, these property requirements can best be satisfied by a suitable segmented copolymer. Soft segments which do not crystallize should provide the elastic recovery power which is required. Hard segments which develop a well-ordered stable crystallite structure should serve as physical crosslinks, thus keeping stress relaxation in the stressed state and hysteresis in the stretching of the crimped fiber at acceptable low levels, and elastic modulus at a high level. The desired strong crystallite structure, however, is usually accompanied by a high melting point. We have found that certain polyurethane segmented copolymers wherein the hard segment is derived from 4,4'-diphenylmethane diisocyanate (MDI) and low molecular weight glycols give a suitable balance between melt stability and crystalline melting point, and can be melt spun to give the desired properties.

Polyurethane block copolymers, more recently called segmented copolymers, were originally developed by Bayer et al.⁶ for casting and conventional rubber processing and later prepared in a form suitable for processing from solution and the melt by Schollenberger et al.,⁷ and with longer hard segments by Pigott et al.⁸ These elastomers are a combination of a soft segment such as an aliphatic polyester or polyether and an aromatic urethane hard segment. The hard and soft segments exist primarily in separate domains, and when the hard segment is of sufficient length, crystalline structure can be developed. The hard segment domains serve as physical crosslinks, providing elasticity and high modulus. Block copolymers, including polyurethanes, were reviewed recently by Estes, Cooper, and Tobolsky,⁹ with emphasis on recent studies of their morphology, and by Allport and Mohajer.¹⁰

EXPERIMENTAL

The model polymers used in this study were prepared from poly(1,4-butylene adipate) (PBA), poly(ethylene adipate) (PEA), polycaprolactone (PCL), or poly-1,4-oxybutylene glycol (PBG), each at a molecular weight of approximately 2000, as the soft segment, and MDI plus 1,4-butanediol as the hard segment. These were prepared at different average hard segment lengths, with the ratio of isocyanate to total hydroxyl groups at the levels of 1.00, 1.02, and 1.04. Polymers are designated U-33, U-43, U-51, and U-54 to indicate average hard-segment contents of 33%, 43%, 51%, and 54%, respectively, by weight, calculated from the total weight of MDI and butanediol used.

Polymers were prepared by standard techniques,¹¹ first degassing 200 g polyester or polyether, each with hydroxyl number about 54 and acid number less than 1, for 30 min at 120°C/50 mm. The weight of polyol was again determined, and the desired weight of vacuum-dried 1,4-butanediol was added. The temperature of the mixture was adjusted to 110°C and the desired weight of MDI (60°C) was added, with stirring. When the reaction temperature reached 140°C, the mixture was poured onto a Teflon-coated hot plate preheated to 140°C and removed as solid slabs after 20 min. Samples were stored in sealed polyethylene bags until they were ground. After grinding, they were vacuum dried for 2 hr at 140°C and stored in dry, sealed containers.

The following equipment was used in characterization studies: Instron capillary rheometer; du Pont thermal analyser Model 900 (DSC); Waters Associates gel permeation chromatograph, Model 200 series; Leitz polarizing light microscope; du Pont CEC moisture analyser, Type 26-321A; General Electric XRD-5 diffractometer; and Kratky small-angle x-ray camera.

Gel permeation studies were made using solutions of 0.5 g polymer per 100 ml dimethylacetamide, at 25°C. GPC calibration data were obtained from M_n by osmometry and M_w by light scattering. Intrinsic viscosities were measured in dimethylacetamide at 25°C. In melt viscosity studies, the sample was loaded into an Instron rheometer and allowed to stand for 6 min to permit thermal equilibration. Molecular weight and viscosity data are averages for two samples. In annealing studies, the polymer was held in the rheometer for an additional 10 min at 210°C to give the annealed sample. In measuring the activation energy of flow, samples were heated to 230°C in the rheometer, then measurements were made successively at 230°, 220°, and 210°C.

RESULTS AND DISCUSSION

Molecular Weight and Rheological Properties

The range of model polymers which was prepared in this study is shown in Table I, along with molecular weight properties. Similar polymers have been described in the literature before, usually with emphasis on mechanical properties. Thus, in the PEA series, U-30 to U-66 polymers have been reported,^{12,13} and their bulk properties were correlated with the hard segment content.¹⁴ In the PBA and PBG series, U-33 polymers have also been described.^{15,16}

With reference to the data in Table I, it is not surprising that the M_w/M_n ratio of these polymers is not 2.0, as is usually predicted for equilibrium polycondensation reactions. Polyurethane formation is not expected to be a true

TABLE I
 Polyurethane Properties, As Prepared

Soft segment	Hard segment, wt-%	NCO/OH ratio	GPC			$[\eta]$	Gel content, %
			M_n	M_w	M_w/M_n		
PBA	33	1.00	30,000	77,000	2.6	0.9	0.1
		1.02	37,000	95,000	2.6	1.1	0.3
		1.04	52,000	148,000	2.8	1.5	9
	43	1.00	33,000	95,000	2.9	1.0	0.3
		1.02	55,000	208,000	3.8	1.7	7
		1.04	—	—	—	1.7	30
	51	1.00	39,000	129,000	3.3	1.2	15
		1.02	—	—	—	1.2	20
		1.04	—	—	—	1.4	50
54	1.00	27,000	74,000	2.7	0.9	0.2	
	1.02	—	—	—	2.2	11	
	1.04	—	—	—	—	72	
PEA	43	1.00	27,000	78,000	2.9	0.8	0
		1.02	29,000	87,000	3.0	0.8	0
PCL	43	1.00	28,000	80,000	2.9	0.8	0
		1.02	39,000	148,000	3.8	1.3	0
PBG	43	1.00	31,000	92,000	3.0	1.1	0
		1.02	34,000	118,000	3.5	1.4	0

equilibrium polycondensation, due to the many side reactions which can consume isocyanate groups. Branching reactions, in particular, such as allophanate, biuret, and isocyanurate formation may be expected in polymerizations such as this, as well as minor amounts of carbodiimide formation. These side reactions should be more extensive as the NCO/OH ratio is raised, thus accounting for the higher molecular weights at the higher ratios.

Similar properties of the same polymers after extrusion from an Instron melt rheometer are shown in Table II. Extrusion essentially eliminated the gel content which was apparent in many of the original polymers prepared at the higher NCO/OH ratios, suggesting that most of the original branch points were thermally sensitive, such as allophanate or biuret. Extrusion also reduced the average molecular weight values when no gel was originally present and in nearly every case resulted in a narrower molecular weight distribution. The water content of the polymers at the time of extrusion was analyzed as 0.02–0.04% for all samples. Thus, thermal degradation, especially dissociation of allophanate groups, and hydrolysis combined are assumed to account for the loss in molecular weight which occurred on extrusion.

Increasing the NCO/OH ratio led to higher average molecular weights in every case, and also to broader molecular weight distributions. The relationship between \bar{M}_w and \bar{M}_n for both original polymers and after extrusion at 230° for the PBA series is shown in Figure I. Data from the PEA, PCL and PBG series fit essentially the same plot.

These results on molecular weight effects in the original polymers are complicated by the fact that increasing the NCO/OH ratio in this range increases molecular weight, and also increases branching, to the extent of large gel contents in extreme cases. While the gel was eliminated by extrusion, one should not assume that all branching was destroyed by extrusion. We were not able to isolate

TABLE II
 Polyurethane Properties After Extrusion^a

Soft segment	Hard segment, wt-%	NCO/OH ratio	GPC		
			\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
PBA	33	1.00	22,000	53,500	2.4
		1.02	23,000	59,000	2.6
		1.04	32,000	89,000	2.8
	43	1.00	24,000	57,000	2.4
		1.02	29,000	72,500	2.5
		1.04	32,000	107,000	3.3
	51	1.00	26,000	68,000	2.6
		1.02	34,000	103,000	3.0
		1.04	58,000	200,000	3.5
	54	1.00	21,000	52,000	2.5
		1.02	29,000	82,000	2.8
		1.04	43,500	141,000	3.2
PEA	43	1.00	27,000	72,000	2.7
		1.02	29,000	90,000	3.1
PCL	43	1.00	26,000	68,000	2.6
		1.02	30,000	92,000	3.1
PBG	43	1.00	27,000	83,000	3.1
		1.02	32,000	113,000	3.5

^a 230°C, 149 sec⁻¹ shear rate.

the effects of increasing molecular weight, without the possibility of increases in branching in this study.

Melt viscosities at 230°C increased as the hard segment content was increased. This trend was consistent, though one must take into consideration differences in molecular weight and branching in making comparisons. Of the PBA-based samples, the comparison with the least effect of molecular weight differences (after extrusion) is shown in Figure 2. A plot of \bar{M}_w (after extrusion) versus melt viscosity for four hard-segment levels in the PBA series, each at several molecular weights, is shown in Figure 3. A line with the theoretical slope of 3.4 is included in Figure 3 for comparison. The deviation from this slope, which is considerable at the higher molecular weights, is believed to be due primarily to the fact that viscosity measurements were not made at zero shear rate. Viscosities of the higher molecular weight samples would have been considerably greater at zero shear rate.

Figure 4 shows a plot of \bar{M}_w (after extrusion) versus melt viscosity for the PEA, PCL, and PBG series. While the differences are not conclusive, they are suggestive of three separate families of data. The higher viscosities of the PBG-based polymers are consistent with other evidence of sharper phase separation in polyether-based segmented polyurethanes, compared to those from polyesters. (Phase separation is discussed in more detail in later sections of this paper.) The data from the PCL series are essentially identical to those from PBA (Fig. 3). The PEA series has the lowest melt viscosity at a given \bar{M}_w and also the highest ester group concentration in the soft segment. Thus, PEA may be expected to be the best solvent for the hard segments, giving the poorest phase separation and lowest viscosity.

The melt viscosity of the U-33 sample based on PBA (NCO/OH = 1.0) was measured at constant shear stress of 10⁶ dynes/cm² at 230°, 220°, and 210°C.

The three points fell essentially on a straight line in an Arrhenius plot, giving an activation energy of flow of 29 kcal/mole. As the NCO/OH ratio was raised, leading to higher molecular weight and more branching, the activation energy for flow increased to 38 kcal/mole for U-33 polymer of \bar{M}_w 84,000/ \bar{M}_n 31,000

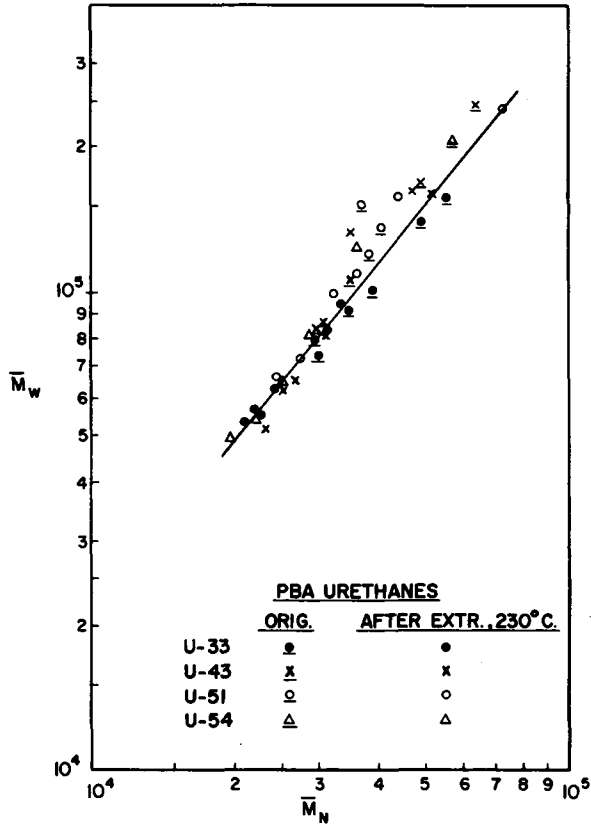


Fig. 1. Molecular weight distributions of PBA polyurethanes, unmelted polymers and after extrusion at 230°C: (●) U-33; (×) U-43; (○) U-51; (△) U-54 after extrusion; (●), (×), (○), and (△) original polymers.

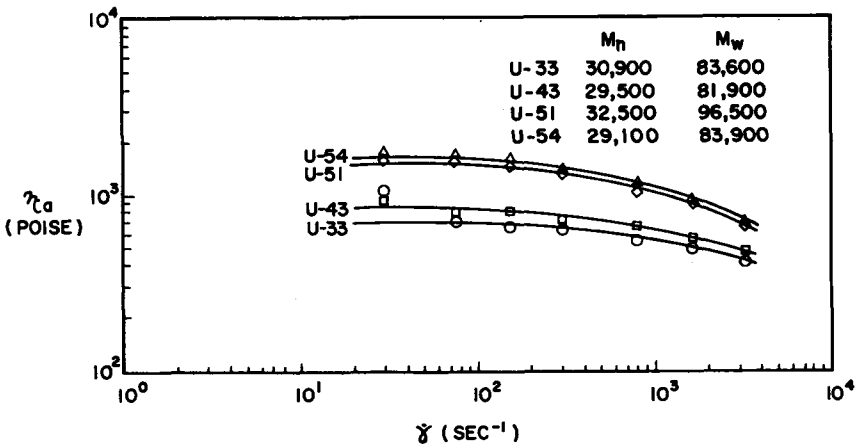


Fig. 2. Melt viscosities of PBA polyurethanes vs. shear rate, at 230°C.

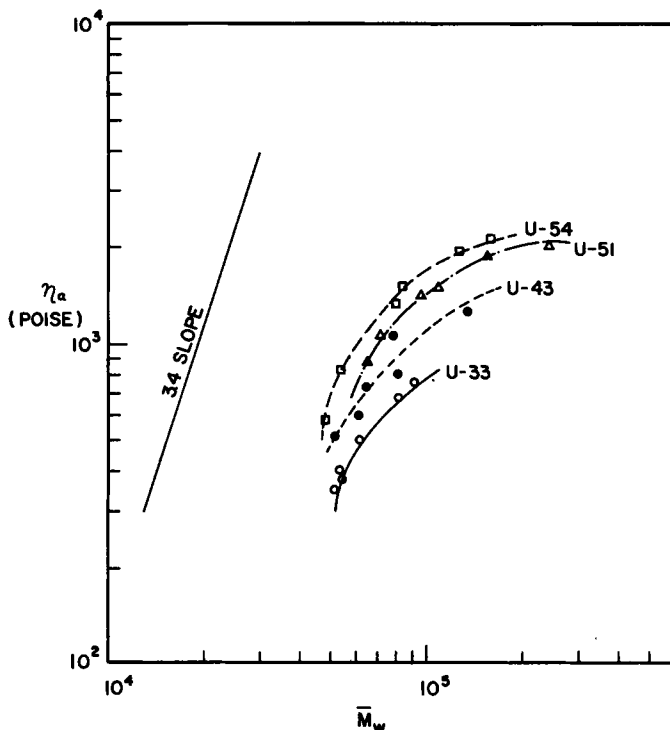


Fig. 3. Melt viscosity of PBA polyurethanes, vs. \bar{M}_w after extrusion at 230°C and shear rate of 149 sec⁻¹.

(after extrusion). Similar trends were noted with other series of polymers, with activation energy increasing as the hard segment content increased. These values, which are rather high, are similar to those observed with styrene-butadiene-styrene block copolymers, where an activation energy of flow of 19 kcal/mole was observed for polymers with less than 31% styrene, and 38 kcal/mole at 35% and higher styrene contents.¹⁷

The significance of the high activation energy of flow of the segmented polyurethanes is readily apparent when one compares it with the value of 12.8 kcal/mole determined for nylon 6. This difference in response to temperature changes is a distinct problem in spinning biconstituent fibers from these polymer types.

Thermal and X-Ray Analysis

The thermal analysis of these polymers extends work of earlier investigators with similar segmented polyurethanes. Extensive thermal analyses of U-33/PBA and U-33/PBG polymers were reported by Clough and Schneider,¹⁶ of U-33/PBA and U-43/PEA by Miller and Saunders,¹⁸ and U-30 to U-55/PEA by Hеспе et al.¹³ Huh and Cooper have studied hard segment contents to about U-43 with varying molecular weight soft segments.¹⁹ Thermal analyses of PEA, PBA, PBG, and the polyurethanes from MDI plus 1,4-butanediol and from MDI plus PBA have also been described, along with correlations of thermal transitions in the copolymers with those in the soft-segment polymers and in the MDI/PBA and MDI/butanediol polymers.¹⁸ With this additional study, rather complete data are now available on the thermal analysis of copolymers of these structures.

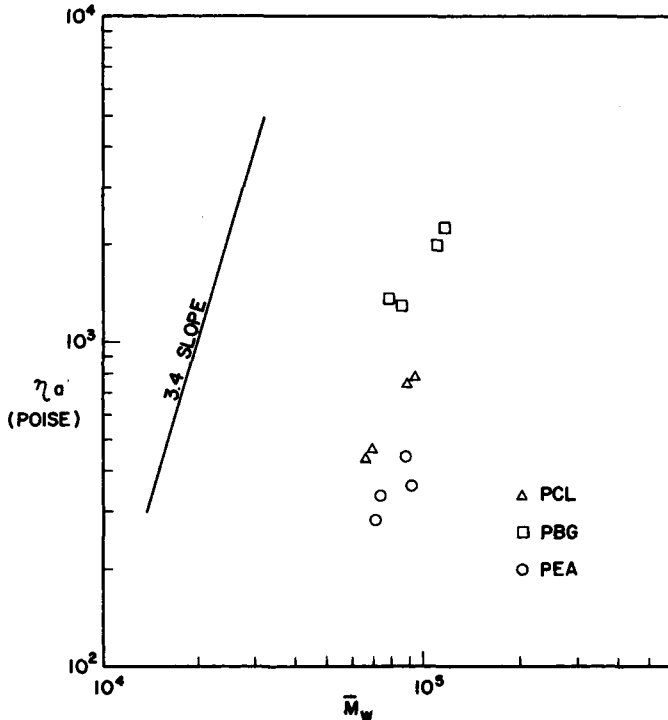


Fig. 4. Melt viscosities of PEA, PCL, and PBG polyurethanes at 230°C and 140 sec⁻¹ shear rate, vs. \bar{M}_w after extrusion.

As indicated in Table III, increasing the NCO/OH ratio generally led to lower melting points, as would be expected if the excess isocyanate resulted in branch points in the hard segments. At the U-43 level, changes in the soft segment resulted in a somewhat higher melting point for the PEA and PCL series than for PBA in the samples of Table III. However, samples of U-43/PBA prepared at another time showed DSC endotherms of 204° and 206°C for two samples, so these differences are believed to be simply due to small variations in the thermal history during preparation. The higher melting point of the original U-43/PBG samples is believed to be significant, however. This is in agreement with the infrared studies of hydrogen bonding by Boyarchak et al.,²⁰ who found a more distinct domain separation in polyether urethanes than in polyester urethanes. Bonart and co-workers²¹ reported x-ray evidence in support of this difference as well. No melting points higher than 213°C have been observed in any of these polyester-based polymers without annealing.

Melting points and heats of fusion of our polymers, as prepared, and melting points after annealing for 10 min at 210°C are shown in Table III. Illustrative DSC curves for the original U-33 to 54/PBA samples (NCO/OH = 1.0) and for the same U-54/PBA after annealing for 10 min at 210°C are shown in Figure 5. The original U-54 polymer showed an endotherm suggestive of multiple melting points. After annealing, the endotherm was sharpened and at a higher temperature. A possible endotherm due to soft-segment melting (~40°C) was developed by the annealing, also. These annealing results are fairly typical for the polyurethanes with higher melting points. The U-33 urethanes simply melted under

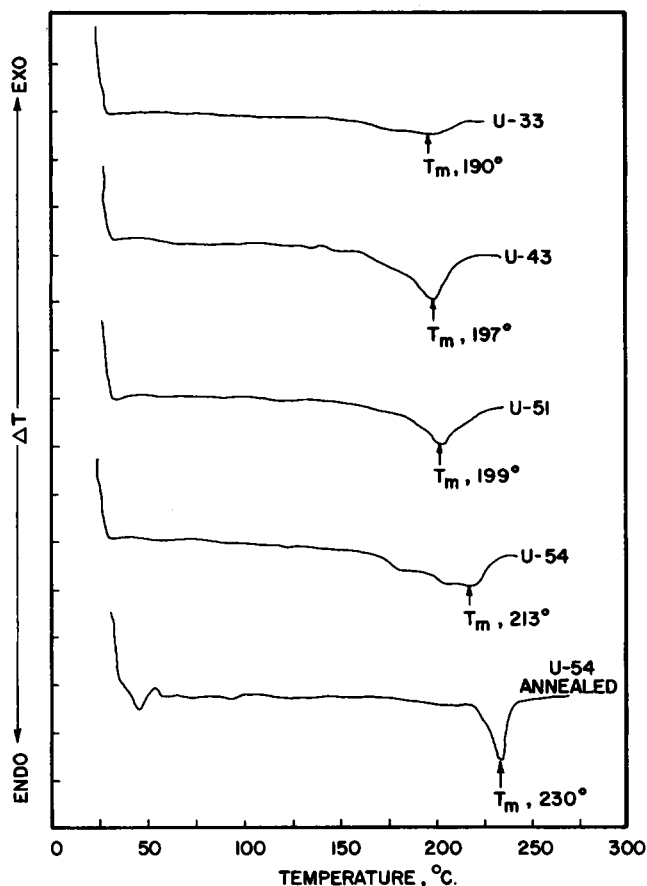


Fig. 5. DSC curves for original U-33 to U-54/PBA polyurethanes and of U-54/PBA after annealing for 10 min at 210°C.

these annealing conditions. Attempts at annealing the U-33/PBA samples at 170°C in the rheometer did not change the original DSC analysis significantly.

In most cases, increasing the hard-segment content increased the DSC melting point and the values for the heats of fusion in the as-prepared polymers. An exception was the U-54/PBA series, where heats of fusion were lower than those for U-43 and U-51 polymers. It may be that at the highest hard-segment contents, the polymerization temperature (140°C) was not high enough to provide adequate segmental mobility to develop as good crystalline structure as was obtained in the U-43 and U-51 samples.

Annealing raised the melting point of all U-43 to U-54 polymers to about 223–230°C, with greater hard-segment contents giving slightly higher melting points. It is not sure that the observed differences are significant, since optimum annealing conditions probably were not used. Extrusion from the rheometer at 210°C, after annealing, may well have caused some loss in crystalline structure.

Also for the original U-33 to 54/PBA series, the lack of any endotherm below 180°C indicates no significant soft-segment crystallinity. Thus, the wide-angle x-ray diffraction patterns for these polyurethanes, exemplified in Figure 6, are believed to result from structural organization in the hard-segment domains.

The presence of only two reflections at 4.6 Å and 3.8 Å *d*-spacings suggests a less than three-dimensional crystalline order. These spacings are in good agreement with two of the three spacings reported by Huh and Cooper¹⁹ for the polymer from MDI and 1,4-butanediol: 4.55, 4.05, and 3.78 Å.

TABLE III
Polyurethane DSC Analyses

Soft segment	Hard segment, wt-%	NCO/OH	As-prepared		Annealed
			T_m , °C	ΔH_t , cal/g	T_m , °C
PBA	33	1.00	189	2.1	None
		1.02	189	2.8	None
		1.04	186	2.4	None
	43	1.00	198	6.0	227
		1.02	195	5.3	None
		1.04	185	4.0	None
	51	1.00	200	7.2	227
		1.02	197	6.6	227
		1.04	195	8.4	229
	54	1.00	213	5.1	230
		1.02	190	3.2	228
		1.04	188	4.2	226
PEA	43	1.00	207	4.4	224
		1.02	205	4.5	223
PCL	43	1.00	208	4.2	224
		1.02	206	3.6	225
PBG	43	1.00	220	3.9	222
		1.02	224	3.9	224



Fig. 6. Wide-angle x-ray scattering of U-51/PBA polyurethane.

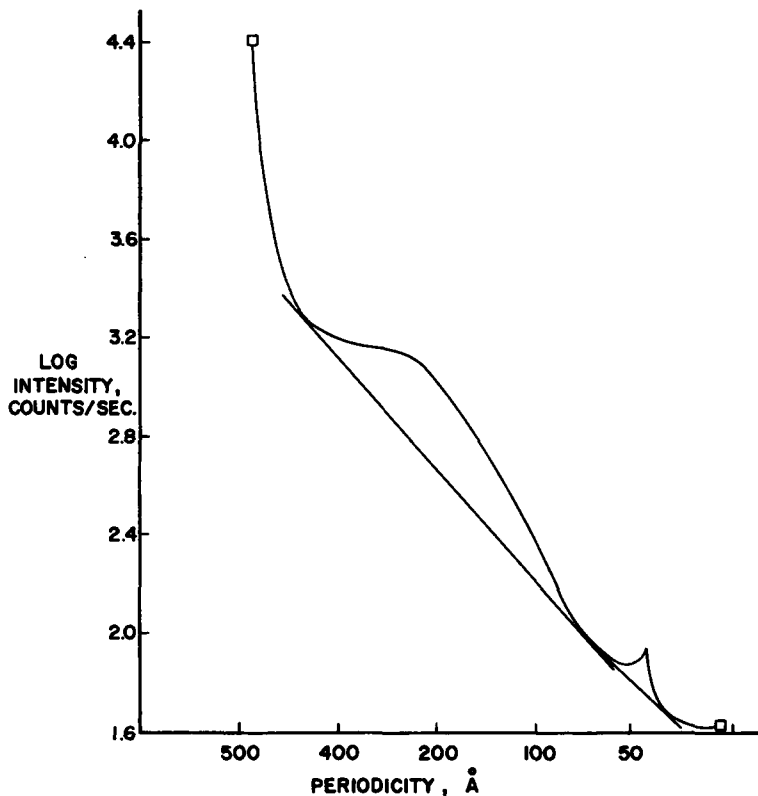


Fig. 7. Small-angle x-ray scattering of U-43/PBA polyurethane.

The small-angle x-ray scan shown in Figure 7 contains two periodicities observed in all of the U-33 to 54/PBA series: one at $46 \pm 4 \text{ \AA}$ attributed to the hard-segment repeat unit in the urethane domains, and the other of approximately $200 \pm 40 \text{ \AA}$ believed to represent an average combined hard- and soft-segment domain size. Bonart and co-workers² also found a small-angle x-ray scattering periodicity of 200–300 Å for a U-33 sample and reported that the repeat distance for one MDI-butanediol unit was 20.29 Å.

Spherulite Observations

Polarized light photomicrographs of unannealed samples prepared from PBA are shown in Figure 8. All samples of U-33 and U-43 polymers showed the less well-organized ("wheat sheaf") structure of Figure 8A and 8B, while those of U-51 and U-54 showed well-developed spherulitic structures. Some U-51 and U-54 samples showed a combination of both degrees of ordering. As already indicated by DSC and x-ray results, the crystalline structures contributing to the order seen in the polarized light photomicrographs are attributed to the hard segments of these polyurethanes. As a further check on this, however, similar observations were made at 70°C, well above the crystalline melting points of the soft segments used. No significant change in the photomicrographs was seen, confirming that the order was due to the hard segments. These photomicrographs are unusual examples of evidence for spherulite formation in elastic polyurethanes with high hard segment content of this structure. Similarly well-

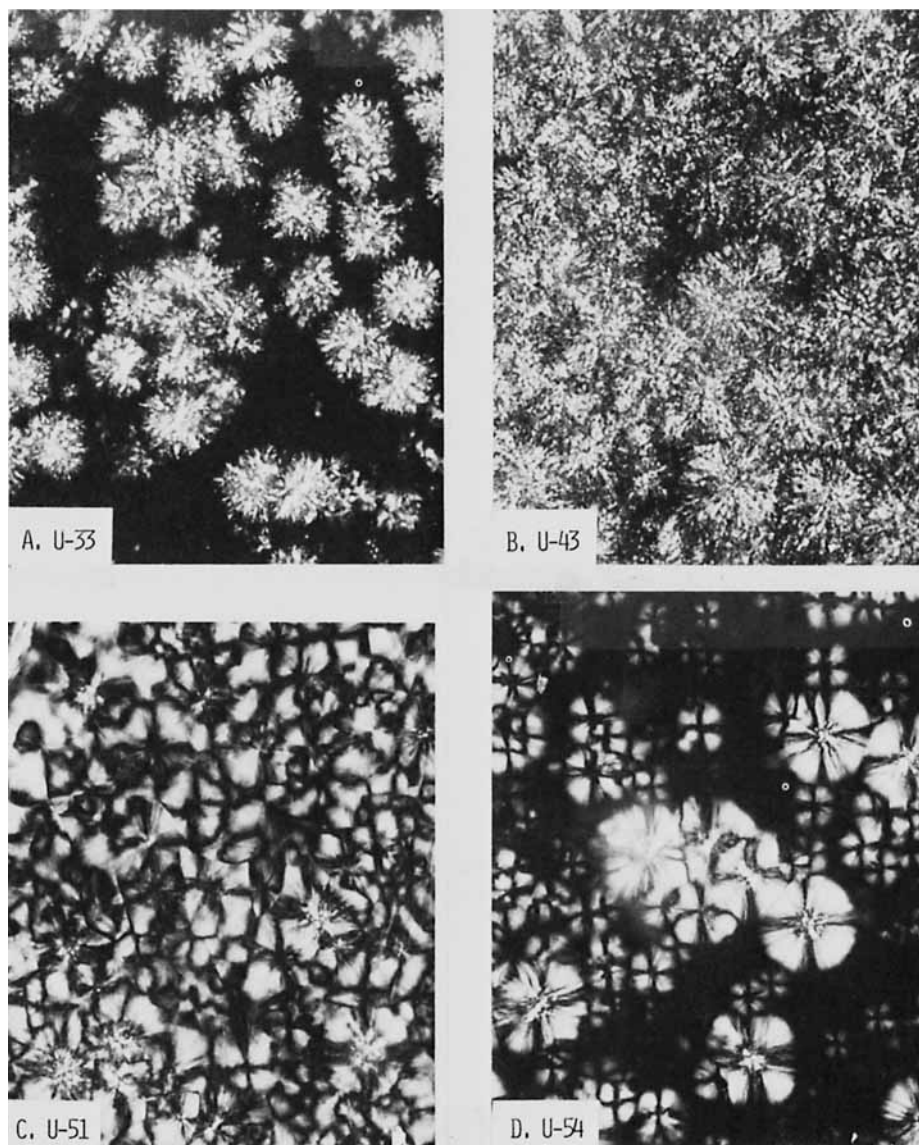


Fig. 8. Polarized light photomicrographs, $320\times$: (A) U-33/PBA, $\text{NCO/OH} = 1.00$; (B) U-43/PBA, $\text{NCO/OH} = 1.04$; (C) U-51/PBA, $\text{NCO/OH} = 1.02$; (D) U-54/PBA, $\text{NCO/OH} = 1.00$.

organized spherulite structure has been found previously, however, in low-melting polyesters or polyethers which are used for soft segments in polyurethanes. For example, Lipatov et al.²² showed similar photomicrographs of spherulites from MW 2000 poly(ethylene adipate). Samuels and Wilkes²³ have reported faint maltese cross patterns in polarized light photomicrographs of segmented polyurethanes having different hard segments in which hydrogen bonding is not possible. These authors²³ also proposed models for spherulitic structures of segmented copolymers, incorporating both the hard- and soft-segment domains in the spherulite.

SUMMARY

The introduction of a new biconstituent fiber, a side-by-side conjugate of nylon 6 and a polyurethane elastomer, has required the solution of a range of technical problems. The nature of some of the major difficulties has been outlined; some of these have been solved by the choice of a suitable polyurethane, and others required engineering solutions.

Two series of model polyurethanes which can be melt spun conjugately with nylon 6 as well as their characterization by several techniques have been described. One series had constant soft segment, MW 2000 poly(butylene adipate), and varying lengths of hard segments derived from 4,4'-diphenylmethane diisocyanate and 1,4-butanediol. The other had 43% by weight hard segment of the same composition, but varying soft segments of MW 2000: poly(ethylene adipate), polycaprolactone, and poly-1,4-oxybutylene glycol. Molecular weights and melt viscosities were measured on the polymers as prepared and also after extrusion at 230°C at several shear rates. The polymers were moderately stable under these extrusion conditions, losing about 10–35% of the number-average molecular weight in most cases. Polymers prepared at 1.02 and especially at a 1.04 NCO/OH ratio usually contained some gel (insoluble in dimethylacetamide), but after extrusion these polymers were completely soluble. The \bar{M}_w/\bar{M}_n ratios varied from about 2.5 at lower molecular weights to about 3.3 at higher molecular weights.

The melt viscosities of the polyurethanes increased with increasing hard-segment content and also with a combined increase in molecular weight and branching. No quantitative measure of branching was obtained, and the effects of molecular weight changes could not be isolated from probable changes in branching. The activation energies of flow were much higher than for nylon 6 (12.8 kcal/mole), ranging from 29 kcal/mole to about 38 kcal/mole as molecular weight, branching, and hard-segment content were increased. Changes in the soft-segment structure showed a small apparent effect on melt viscosity at constant molecular weight, with viscosities decreasing in the order PBG > PCL \approx PBA > PEA.

Morphologic studies included thermal, x-ray, and polarized light experiments. There was no evidence for crystallinity of the soft segments in the polymers as prepared. Thermal analyses (DSC) and wide-angle x-ray scattering indicated crystallinity due to the hard segments, with small-angle x-ray scattering indicating a size of about $200 \pm 40 \text{ \AA}$ for the average combined hard- and soft-segment domains. Hard-segment crystalline melting points (DSC) increased with increases in hard-segment content in the as-prepared polymers and ranged as high as 230°C after annealing. Melting points of freshly prepared polymers were somewhat higher when the soft segment was PBG, rather than the polyesters, which supports earlier indications of sharper phase separation between hard- and soft-segment domains when polyethers are used, compared to polyesters. The small effect of soft-segment structure on melt viscosity cited above may also be a manifestation of this difference in hard- and soft-segment phase separation. Polarized light photomicrographs indicated a wheat sheaf structure with 33% and 43% hard-segment content and well ordered spherulite structure at 51–54% hard-segment content.

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