

Thermal and mechanical properties of solution polymerized segmented polyurethanes with butadiene soft segments

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A series of HTPBD containing polyurethanes of high molecular weight have been synthesized in solution. The value of the soft segment T_g is very close to that of the free HTPBD and independent of hard segment content indicating complete or very nearly complete phase segregation. Since the hard segments of TDI/BDO are amorphous, the driving force for phase segregation must arise from the large degree of incompatibility between the polar hard segment and nonpolar soft segment. Furthermore, in these samples there is also no opportunity for hydrogen bonding between hard and soft segments to enhance compatibility.

The values of the hard segment glass transition increase with the average hard segment length following a Fox-Flory type relationship. In contrast to the segment T_g observed in bulk polymerized samples, only a single hard segment T_g occurred in the present study. This indicates that the double T_g behaviour is a result of the heterogeneous nature of the bulk polymerization.

With increasing hard segment content, the properties vary from soft to rigid elastomers, and rubber roughened plastics. This variation in properties is caused by changes in the sample morphology which depends upon the relative fractions of hard and soft segments. Mechanical properties show marked improvement over the corresponding bulk polymerized samples. Unlike polyester and polyether urethanes, these materials evidence no change in the soft segment T_g following thermal treatment and no effect of thermal history on the mechanical properties.

(Keywords: solution polymerized segmented polyurethanes; soft segment; hard segments; phase segregation)

INTRODUCTION

Segmented polyurethanes are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments and subsequent phase separation into separate domains. The soft segment is usually a polyether or polyester of molecular weight between 1000 and 5000 possessing a glass transition temperature (T_g) well below ambient temperature. Hard segments are typically formed by the extension of an aromatic diisocyanate with a low molecular weight diol or diamine and have a T_g or melting transition above the used temperature. The hard segment domains provide physical crosslinking, act as reinforcing fillers and are responsible for the performance of these materials at higher temperatures.

The existence of phase segregation, caused by the clustering of hard and soft segments into separate micro domains, has been well documented for block copolymers and segmented polyurethanes¹. Therefore physical and mechanical properties are interpreted on the basis of a two phase model. Most polyurethane studies are complicated by one or more of the following effects: (1) specific interactions between phases via hydrogen bonding, (2) crystallinity in either phase, and (3) the presence of

chemical crosslinking. All three effects may influence the nature and extent of phase segregation.

These complications were avoided by using a hydroxy terminated polybutadiene (HTPBD) with exact difunctionality and a hard segment consisting of 2,4 toluene diisocyanate (TDI) and butanediol (BDO). The nonpolar soft segment prevents interphase hydrogen bonding and its high vinyl content (55%) prevents crystallization. The unsymmetrical TDI prevents crystallization in the hard segment². There is a large difference in solubility parameters between the hard and soft segments; $\delta = 8.1$ – 8.4 (cal cm⁻³)^{1/2} for polybutadiene³ and $\delta = 12.2$ (cal cm⁻³)^{1/2} for TDI/BDO hard segments⁴. Therefore, a high degree of phase segregation would be expected for this polyurethane.

The polyurethanes described above were previously synthesized in this laboratory via a two step bulk polymerization method⁵. The HTPBD was first end-capped with TDI, following which BDO was added. The reactants were mixed and then poured into a mould for complete curing. A 5% excess of TDI was used in all cases. As expected, highly phase segregated materials were obtained. Thus, the soft segment T_g was invariant with hard segment content and very close to that of the free HTPBD. The hard segment T_g behaviour proved to be

unexpectedly complicated. Two T_g values were detected in some samples instead of a single transition. The same phenomenon has been observed in other HTPBD based polyurethanes^{6,7}. It was suggested that the two T_g values correspond to domains of different hard segment lengths. However, it remained unclear why the hard segments would segregate into separate domains based on hard segment length.

To better understand the behaviour, Xu *et al.*⁸ have performed fractionation studies to obtain sol-gel fractions from these samples in DMF at 70°C. The samples were completely soluble only in DMF above 85°C, possibly because of the cleavage of allophanate crosslinks that have been detected in these samples by Fu⁹. For all samples studied, the gel fraction had a hard segment content and length, calculated from i.r. measurements, which was of constant value, independent of the original composition and correspondingly a single hard segment T_g . Hard segment content, length, and T_g of the sol fractions varied systematically with the original sample composition. The results suggest that a bimodal distribution of hard segment lengths occurs in these copolymers. Chen *et al.*¹⁰ followed the bulk polymerization of these materials by optical microscopy. The reactant mixture was placed between glass slides, kept at the reaction temperature, and observed under partially crossed polars (70°). Domains, thought to be BDO rich regions, were present at the beginning and throughout the reaction. Therefore, the final composition is thought to be controlled by the diffusion rates of the reactants between domains and by the reaction rates of the species. A model based on the observed phase separation and on the diffusion of reactants was presented to explain the formation of a bimodal distribution of hard segment lengths.

Phase separation has also been found to occur at low conversion in other polyurethane bulk polymerizations^{11,12}. Camargo *et al.*¹¹ found that phase separation occurs at a short characteristic hard segment length in uncatalysed RIM polyurethane systems. His data for the hard segment length at phase separation are in agreement with the d.s.c. data of Hager *et al.*¹².

Products formed by this bulk polymerization are generally opaque and exhibit poor mechanical properties. Molecular weights are below 10 000 and $\bar{M}_w/\bar{M}_n = 3-7$ ¹³. Furthermore, they contain allophanates, the formation of which is facilitated by the high reaction temperature and the use of an excess amount of isocyanate. To avoid the premature phase separation which occurs in the bulk reaction and the resulting poor mechanical properties it seemed desirable to carry out the reaction in solution. This should allow for a homogeneous reaction mixture. Additionally, allophanate formation should be suppressed since stoichiometry is maintained and the reaction temperature used is lower than in the bulk polymerization. The present study focuses on the solution synthesis and properties of a series of HTPBD polyurethanes. The results of d.s.c., dynamic mechanical, and tensile measurements on these polymers are reported.

EXPERIMENTAL

Materials

HTPBD of molecular weight 2200 was kindly supplied by the Japanese Synthetic Rubber Co. It has a function-

ality of 1.97 and a microstructure consisting of 55% vinyl, 35% *cis* and 10% *trans* double bonds as reported previously⁵. 2,4-TDI (ICN: containing 5-10% 2,6 isomer) and BDO (Aldrich) were vacuum distilled and used within two months. Tetrahydrofuran (THF), HPLC grade, was refluxed overnight in the presence of isocyanate and distilled immediately prior to use. Dibutyl tin dilaurate (DBTDL), (Alfa) was used as received.

Two to seven grams HTPBD were dissolved in 50 ml CHCl_3 in a 200 ml round bottom flask equipped with a magnetic stirrer and nitrogen inlet. The CHCl_3 was distilled off as an azeotrope to remove any adventitious water. 100 ml THF and 2 drops DBTDL catalyst were added and the solution was brought to reflux. The final desired stoichiometric amount of TDI was added followed by 1 h or reaction to encap the HTPBD. The amount of BDO added was calculated to reach a final isocyanate/hydroxyl ratio of 1. It was added stepwise over 2-3 h followed by 1.5 h of reaction. The total concentration was about 10% and the solution remained clear throughout the reaction. The polymer was precipitated in distilled water and dried in vacuum for 24 h at 70°C.

Measurements

Differential scanning calorimetry (d.s.c.) was performed with a Perkin-Elmer DSC-II. A heating rate of 20° min^{-1} and a sensitivity of 2 or 5 mcal s^{-1} were used. Samples of approximately 15 mg were prepared by compression moulding at 120°C for 15 min. The glass transition temperature (T_g) was taken as the onset of the step increase in heat capacity.

Dynamic mechanical measurements were performed with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). The temperature range of -90°C to 130°C was scanned at 5° min^{-1} at 1 Hz. A double cantilever bending geometry was used. Samples 1.5 mm thick were compression moulded at 150°C for 30 min.

Stress-strain data were obtained on an Instron universal testing machine at an extension rate of 1 cm min^{-1} using a gauge length of 2.5 cm. Rectangular samples 3 mm wide were cut from 0.5 mm thick films compression moulded at 120°C for 30 min. Results are averages of at least 5 different samples.

RESULTS AND DISCUSSION

Sample characterization

The appearance of samples obtained from this solution polymerization differs from that of the bulk polymerized samples. Whereas the latter are generally yellow and opaque, the solution polymerized samples are white and produce clear films when compression moulded. Solution polymerized samples are completely soluble in THF at room temperature in contrast to the low temperature insolubility of the bulk polymerized samples. The complete solubility is taken as evidence for the expected absence of allophanate crosslinks due to the low reaction temperature (68°C) and the use of exact stoichiometric amounts of reactants as well as the homogeneous reaction conditions.

Table 1 presents the compositions and some characteristic properties of the samples studied. The molar ratios of reactants, HTPBD:TDI:BDO, is completely described by 1: N :($N-1$) and only the value of N need be specified. Molecular weights were determined from g.p.c. data using

Table 1

Sample	Molar ratio TDI/HTPBD	Percent hard segment	\bar{M}_n	Properties
JSR10	1.0	9	11,000	Viscous liquid
JSR23	2.3	20	28,000	Clear, soft, very tacky rubber
JSR33	3.3	27	23,000	Clear, tacky soft rubber
JSR45	4.5	34	41,000	Clear, tough rubber
JSR58	5.8	41	24,000	Clear, tough rubber
JSR68	6.8	44	60,000	Clear, tough rubber
JSR87	8.7	51	35,000	Clear, rubbery, tough
JSR104	10.4	56	28,000	Clear, rubbery, tough
JSR253	25.3	76	18,000	Clear, rigid

Table 2

Sample	M_n of hard segment	T_g hard segment		T_g Soft segment	
		d.s.c.	DMTA	d.s.c.	DMTA
HTPBD	0	--	--	-68	--
JSR10	174	--	--	-61	--
JSR23	440	-27	--	-62	-32
JSR33	781	6	55	-63	-32
JSR45	1098	30	64	-63	-30
JSR58	1441	33	68	-63	-32
JSR68	1795	45	99	-63	-31
JSR87	2207	43	91	-63	-32
JSR104	2656	50	99	-63	-32
JSR253	6576	63	103	-65	-32
Hard segment homopolymer	60,000	73	--	--	--

a calibration curve for polystyrene. The \bar{M}_n of the solution polymerized samples are generally an order of magnitude greater than the \bar{M}_n of the corresponding bulk polymerized samples. The polydispersity index (\bar{M}_w/\bar{M}_n) of the solution polymerized samples is about 2, which is the expected value for step growth polymerizations, while the indexes for the bulk polymerized samples range from 3 to 7. The final column gives information about the general physical appearance and the mechanical nature of these samples.

The two step solution polymerization is a procedure for which Peebles¹⁴ has devised a method to calculate the average hard block length and hence the average molecular weight of the hard blocks. The values thus calculated are included in Table 2.

D.s.c.

D.s.c. traces of some samples are presented in Figure 1. Single hard and soft segment T_g values were observed for these samples confirming the two phase nature of this system. A summary of the d.s.c. transition temperature for the copolymers, HTPBD, and hard segment homopolymer are presented in Table 2. The soft segment T_g is independent of hard segment content and thermal history as in the bulk polymerized samples. The T_g of $-63^\circ\text{C} \pm 2^\circ$ is only 5° above that of the free HTPBD. Camberlin and Pascault¹⁵ have calculated that an increase in T_g of 4° of the soft segment above the corresponding homopolymer T_g corresponds to complete phase segregation. Greater differences in the T_g values correspond to increasing amounts of phase mixing. Our results indicate that phase

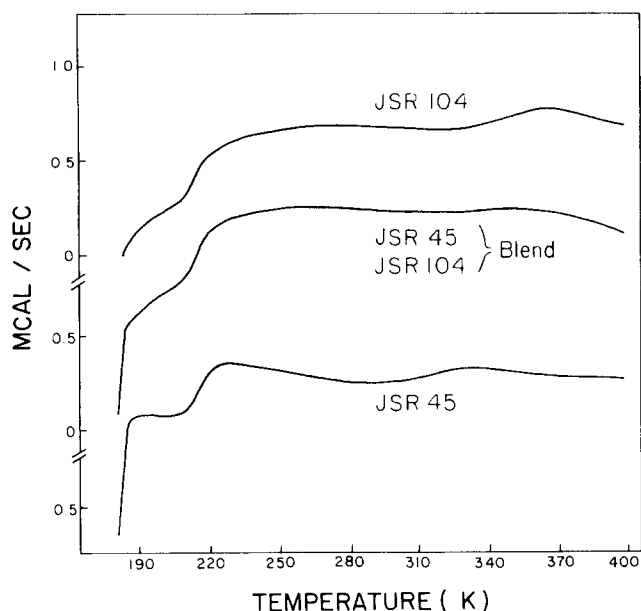
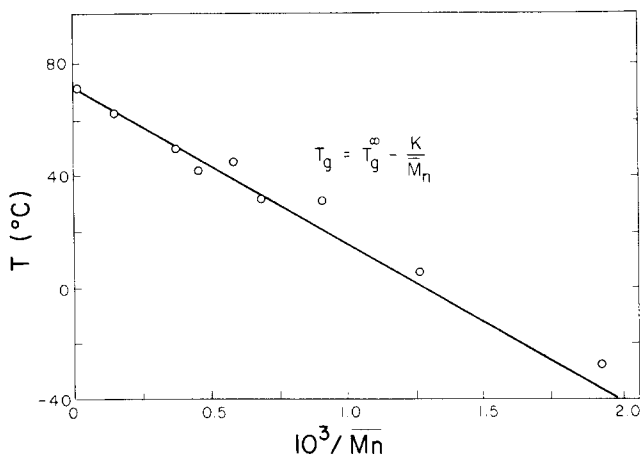


Figure 1 D.s.c. traces for samples JSR 23, 58 and 104


 Figure 2 Dependence of hard segment glass transition temperature on $1/\bar{M}_n$

segregation, in these samples, is complete or very nearly so.

In contrast to the bulk polymerized samples, single hard segment T_g values were observed in all samples. The T_g have been plotted versus the inverse of the hard block molecular weights (from Table 2) in Figure 2. The straight line is described by a relationship analogous to the Fox-

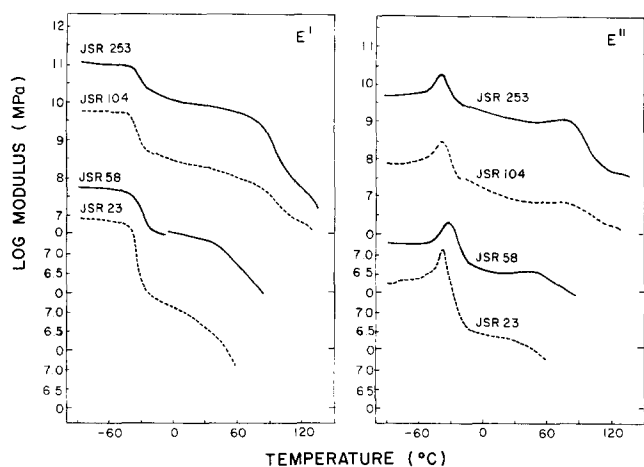


Figure 3 Temperature dependence of E' and E'' for JSR 23, 58, 104, and 253

Flory relationship¹⁶:

$$T_g = T_g^\infty - K/\bar{M}_n \quad (1)$$

where T_g^∞ is the T_g of a hard segment block of infinite molecular weight. The experimental value of the constant is 5.7×10^4 , which is in the range expected for stiff polar polymers¹⁷. A linear relationship between T_g and inverse number average molecular weight of the hard segment has not been observed in other TDI/BDO polyurethane systems¹⁸, but has been observed in a variety of diblock and triblock copolymers¹⁹. The Fox-Flory theory takes into account the differences of the free volumes of the chain ends and inner chain units. In our system chain ends may be neglected but a significant difference in the free volumes of inner block units and block ends is expected since this relationship holds. The HTPBD blocks attached to the ends of each hard segment block are highly mobile at these temperatures and exert little restraint on the hard block ends. Therefore, the hard block ends may behave as free chain ends.

The curve in Figure 2 is roughly parallel to a curve constructed by Fu *et al.*²⁰ for monodisperse 2,4-TDI/BDO oligomers. However, the oligomer T_g occurs at values about 25°–30° higher than for the corresponding average molecular weight hard blocks. This difference is possibly a result of the chemical nature of the hard block endgroups. The oligomers cited here have hydroxyl endgroups which may well be associated through hydrogen bonding, thereby restricting the endgroup motion and raising their T_g . Another possible explanation centres on the presence of short hard segment blocks. Peebles¹⁴ showed that a most probable distribution of hard segment lengths should result from this polymerization method. Therefore, a significant number of short hard segments are present. These short hard blocks might act as plasticizers for longer blocks and lower the T_g of the longer hard segments.

Some bulk polymerized samples displayed two hard segment T_g values. To determine if these arise due to the incompatibility of hard segments of different lengths a blend of JSR45 (hard segment $M_n = 1098$) and JSR104 (hard segment $M_n = 2656$) was prepared from solution and analysed by d.s.c. Equal amounts by weight JSR45 and JSR104 were dissolved in THF and a film was cast. The d.s.c. trace is included in Figure 1. As can be seen, the

blend has a single T_g intermediate between that of the two constituents. This shows that in this system different hard segment lengths are compatible. Therefore, the two T_g values observed by Brunette *et al.*⁵ must arise from the heterogeneous nature of the bulk polymerization.

DMTA

The relaxation behaviour of several of the samples studied is illustrated in Figures 3 and 4. As can be seen, the plots illustrate two relaxations corresponding to the two phases present in the material. The T_g values, determined at 1 Hz from the $\tan \delta$ peaks, are listed with the d.s.c. results in Table 2. Consistent with the d.s.c. results, the soft segment T_g of $-31^\circ\text{C} \pm 2^\circ$ is independent of hard segment content. The value for T_g obtained by DMTA is approximately 30° higher than the value obtained from d.s.c. The soft segment T_g is also characterized by a step decrease in the value of the storage modulus of 1 to 2 orders of magnitude.

The hard segment T_g varies systematically with increasing hard segment content. Samples of lowest hard segment content display only an increase in $\tan \delta$ with increasing temperature to the point of flow ($\tan \delta = 1.2$). Increasing the hard segment content leads first to a shoulder and finally, for JSR253, a sharp peak. This increase of hard segment T_g is a result of increasing hard segment length as discussed for the d.s.c. results. The T_g values, as with the soft segment T_g , are about 30° higher than those determined by d.s.c.

Consistent with findings for other phase segregated systems²¹, the level of the plateau storage modulus above the soft segment T_g increases with increasing hard segment

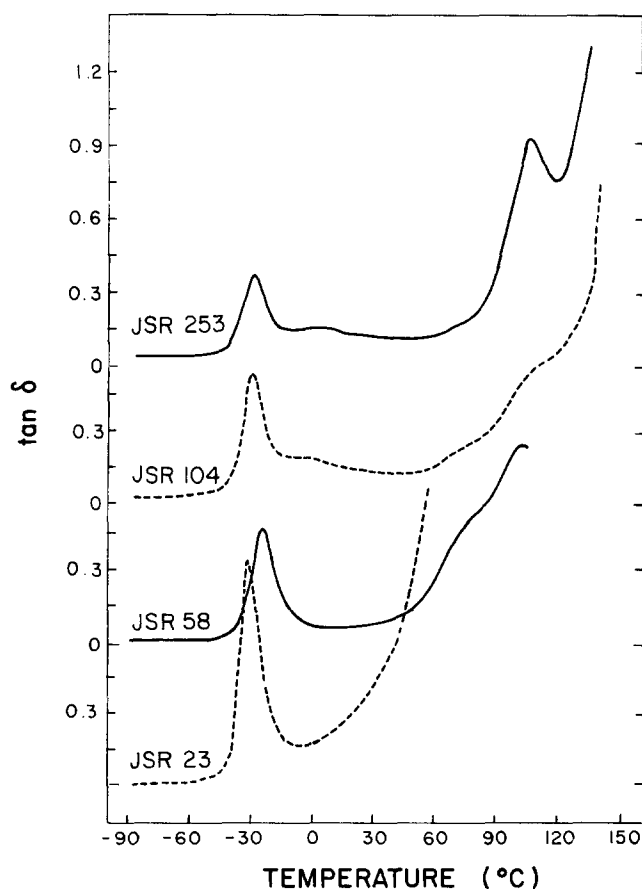


Figure 4 Temperature dependence of $\tan \delta$ for JSR 23, 58, 104, and 253

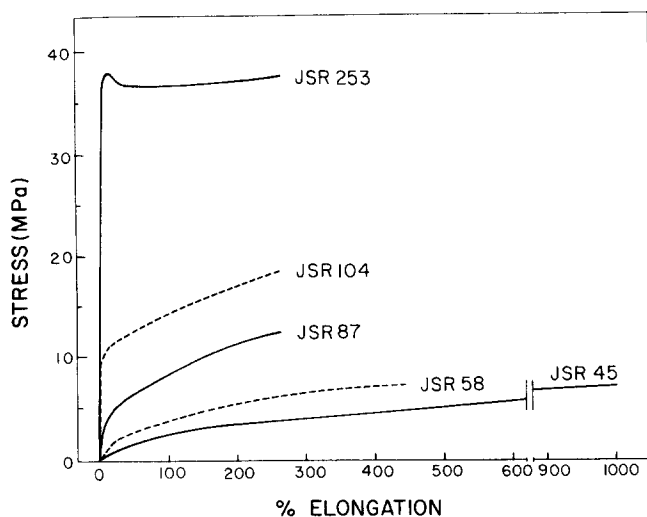


Figure 5 Stress-strain behaviour for JSR 45, 58, 87, 104, and 253

content. This effect can be attributed to an increase in the volume fraction of hard segment. The reinforcing nature of the hard segment domains is responsible for the increase in modulus.

A final point to note lies in the temperature dependence of $\tan \delta$ illustrated in Figure 4. As the hard segment content increases, the magnitude of the soft segment damping peak decreases while the magnitude of the hard segment shoulder or peak increases. Such changes in the damping behaviour of these materials clearly reflect changes in the relative amounts of the constituent phases. The change in hard segment sampling behaviour between samples JSR104 (56% hard segment) and JSR253 (76% hard segment) suggest a change in sample morphology. JSR253 displays a pronounced $\tan \delta$ peak of magnitude close to that of the soft segment damping peak of the lowest hard segment content sample, while JSR104 displays only a shoulder. The plateau modulus of JSR253 is also significantly higher than that of JSR104 (about 0.6 order of magnitude). Given the relative volume or weight fraction hard segment of these samples, a difference in morphology would not be unexpected. Further evidence for a morphological change is presented and discussed later.

Unlike the behaviour of other polyurethanes²², and consistent with the results for other HTPBD polyurethanes^{5-7,23}, the dynamic mechanical properties of these materials are unaffected by thermal history. Samples were quenched from 130°C to -80°C and immediately retested and were also stored at room temperature for a month prior to retesting. The values for the various viscoelastic functions are essentially unchanged. This invariance of properties suggests that no thermally activated phase mixing, altering the sample morphology, occurs. The absence of thermal history effects can be attributed to the lack of urethane hydrogen bonding to the HTPBD soft segment⁵ by the hard segment NH groups.

Tensile measurements

The effect of hard segment content on the stress-strain behaviour of the copolymers was investigated and compared with the results of Brunette *et al.*⁵ for bulk polymerized samples. Stress-strain curves are presented in Figure 5. Three general types of mechanical behaviour

are observed, depending on hard segment contents. Materials with hard segment content below 45% are soft elastomers. At 76% hard segment content they behave as a rubber toughened plastic, displaying necking and strain whitening. Intermediate compositions behave as rigid elastomers. This variation of mechanical properties is very likely caused by changes in sample morphology. When volume fractions of the two phases are similar, both phases may be continuous. The stress-strain data suggest that below 45% hard segment content the polybutadiene rubber soft segment is the continuous phase with hard segment domains acting as physical crosslinks and reinforcing filler. At 76% hard segment content, the hard segment is expected to comprise the continuous phase with domains of the elastomer toughening the material. Intermediate materials appear to be bicontinuous in nature. The deformation of bicontinuous samples proceeds in two steps: first the relatively high modulus hard segment deforms followed by the low modulus deformation of the elastomer after the hard segment becomes discontinuous. Stress-strain curves of these materials display two greatly different slopes corresponding to the moduli of the two phases. These described morphological changes have been observed by electron microscopy²⁴ for these materials. The intermediate compositions appear to have a 'plate like' bicontinuous morphology.

Morphological changes in mechanical properties also occurred in the bulk polymerized samples⁵. The changes in the bulk polymerized sample morphology occurred at lower hard segment contents and over a narrower range of composition than for the solution polymerized samples. Brittle low modulus plastics were obtained at hard segment contents above 45% and soft rubbers were obtained at a hard segment content below 35%.

Values for the stress and elongation at break are listed along with the values obtained for the bulk polymerized samples in Table 3. The same strain rate and sample cross section were used to study both series of samples. The table shows a marked difference between bulk and solution polymerized materials. The solution polymerized materials exhibit tensile strengths which are 2 to 7 times higher than those of corresponding bulk polymerized samples and maintain high elongations at high hard segment content. These differences are the result of the different products obtained by different synthetic routes.

CONCLUSIONS

We have shown that true 'random block' copolymers of hydroxy terminated butadiene oligomers with TDI and BDO can be prepared using a solution polymerization

Table 3 Mechanical properties

Bulk polymerized			Solution polymerized		
Wt. fraction hard segment	σ_B (MPa)	ϵ_B (%)	Wt. fraction hard segment	σ_B (MPa)	ϵ_B (%)
0.18	2.83	1,000			
0.25	4.14	1,620	0.27	10.3	620
0.32	3.31	1,160	0.34	7.53	1,120
0.42	4.27	430	0.41	7.31	440
0.49	2.69	70	0.51	12.4	260
0.55	2.69	15	0.55	18.6	250
			0.76	38.6	250

technique. Previous bulk polymerizations of the same reactants led to very non-uniform products.

The bulk polymerized samples invariably exhibited two hard segment T_g values. The solution polymerized samples exhibited only a single hard segment T_g which was inversely proportional to the \bar{M}_n of the hard segment. The solution polymerized urethanes exhibited higher breaking stresses than the bulk polymerized urethanes at the same nominal hard segment content.

It may be concluded that phase separation during polymerization or as a consequence of the incompatibility of the reactants in 'random block' copolymers may result in very non-uniform products which differ considerably in their properties from those of the structures predicted on the basis of stoichiometry.

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