

Relation of Structure to Properties in Polyurethanes: Effect of Branching

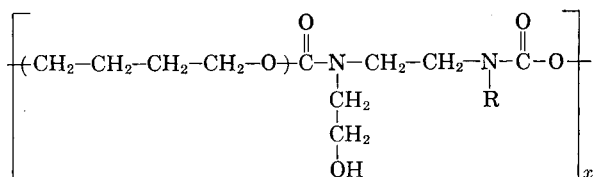
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Correlation of the physical properties of elastomers with their molecular structure depends basically upon the availability of a systematic array of appropriate model polymers. Differences in molecular weight and its distribution, degree of linearity, and structure and distribution of backbone constituents (in copolymers) among others are variables which can affect the physical properties of high polymers. In the classical vinyl polymerization systems control of these factors is at best, crude. However, the recently developed technology for the preparation of urethane block polymers provides the means for the reasonable control of structural details. The chemical reactions involved in the synthesis of polyurethanes are well defined and readily adaptable to the preparation of a variety of elastomers differing systematically in specific structural features. Models necessary for a detailed experimental correlation of physical properties with molecular structure are now a practical reality.

In the present work polyurethane technology has been used to investigate the effects of chain branching on polymer physical properties. Two aspects of chain branching phenomena have been examined: first, the influence of various short chain aromatic branches on the properties of polymers with fixed backbone structure; and second, the influence of "loose ends," or long chain branches, on polymer vulcanizate properties.

For the study of short chain branching, polyether urethanes (I) and (II) were synthesized according to the method described previously.¹



(I) R = H

(II) R = $\text{-(CH}_2\text{)}_3\text{-CH=CH}_2$

Subsequent reaction of the pendant hydroxyl groups with various monoisocyanates provided a means whereby short pendant chains of varying structure and in varying concentration could be attached to a high molecular weight, linear polyurethane backbone. The pendant double bonds in (II) provided cure sites for vulcanization with an accelerated sulfur recipe.

Long chain branching was studied in a series of polyether urethanes which were purposely branched in a controlled manner during the preparation. Condensation of polytetramethyleneether glycol (molecular weight about 1000), trimethylolpropane and 2,4-hexadiene-1-ol with 2,4-toluene-diisocyanate provided branched polymers, the chain ends of which terminated in the 1,3-diene structure. Network formation (vulcanization) was effected by connecting the terminal diene functions through a Diels-Alder reaction with a bisdieneophile, *m*-phenylenebismaleimide. The degree of vulcanization (or effective network chain concentration) was determined by the proportion of triol used in the polymer synthesis and by the number of chain ends connected by the curing agent. Long chain branches were introduced into the vulcanizates by using less than the stoichiometric amount of curative required to connect all the chain ends.

EXPERIMENTAL

The preparation of polyether urethane (II), its curing by an accelerated sulfur recipe, and testing, and the measurement of effective network chain concentration have been described earlier.¹ Polyether urethane (I) was prepared in a similar manner from the bischloroformate of polytetramethyleneether glycol (about 1000 molecular weight) and *N*-(2-hydroxyethyl) ethylenediamine (mole ratio = 1.00:1.03) and had an intrinsic viscosity of 1.05 at 30°C. in a mixture of tetrahydrofuran and dimethylformamide (86.2/13.8, w/w). Both polymers contained pendant hydroxyl groups spaced about 1200 molecular weight units apart through

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which arylurethane groups could be attached by means of reaction with arylmonoisocyanates. In polyether urethane (II), similarly spaced carbon-carbon double bonds were present also, and these served as sites for sulfur curing.

The reaction of monoisocyanates with the pendant hydroxyl groups of polyether urethanes (I) and (II) was carried out in the following manner. To a 22 weight-% solution of polymer in purified tetrahydrofuran (distilled from lithium aluminum hydride) was added the requisite amount of isocyanate. The reaction was catalyzed with an equal weight mixture of ferric acetylacetonate and triethylamine, added as a 1 wt.-% solution in dry benzene. The concentration of catalysts in the reaction solution equalled 2.3×10^{-4} moles of ferric acetylacetonate and 6.6×10^{-4} moles of triethylamine for each mole of hydroxyl groups. After about 48 hr., the isocyanate concentration had dropped to 1-3% of its original value as determined by titration with dibutylamine. The solvent was removed by drowning the mixture in a large excess of water. The coagulated polymers were washed well with water and dried on a chrome-plated, 2×6 in. rubber mill at 105-110°C.

Crystallization rates of the several polymers were measured dilatometrically at 0°C. Solution viscosity measurements were made at 30°C. in a tetrahydrofuran: dimethylformamide mixture (86.2/13.8, w/w) or in benzene using an Ostwald viscometer. Williams plasticity and recovery measurements were made at the specified temperatures according to ASTM test number D 926-47T. Vulcanizate physical properties measured were: Yerzley resilience (ASTM D 945-52T), compression set (ASTM D 395-53T), temperature reaction (ASTM D 1329-54T), and modulus on the Instron tensile testing machine² at a crosshead speed of 20 in./min.

The polyether urethanes used in the study of long chain branching were prepared in the following manner. To a homogeneous mixture of 2,4-hexadiene-1-ol, polytetramethylene ether glycol (about 1000 molecular weight), and trimethylolpropane was added a stoichiometric amount of 2,4-toluene diisocyanate followed by 3 drops of 10% triethylamine solution in acetone and 6 drops of 5% ferric acetyl acetonate solution in benzene per 100 mmole of diisocyanate. After a brief, vigorous stirring, the mixture became warm and was poured into an aluminum "toothpaste tube," sealed, and heated for 16 hr. at 80°C. The range of compositions studied varied from a triol/mono-ol mole ratio of 0.30 to

0.55 and a diol/mono-ol ratio of 4 to 12. Calculations indicate the gel point should be reached when the triol/mono-ol mole ratio = 0.33.³ In practice it was found that soluble polymer was produced when this ratio was as high as 0.40-0.45. Compounding was carried out on a 2×6 in. rubber mill. Stocks were cured at 140°C. for 1 hr. in standard laboratory presses. In all cases, vulcanizate properties were determined on stocks cured with 1.3-3.3 PHR of *m*-phenylene bismaleimide and containing 30 PHR of HAF black.

RESULTS AND DISCUSSION

Short Chain Branching

Short pendant chains of varying structure and in varying concentrations were attached to a high molecular weight, linear polyurethane backbone by reaction of various aryl monoisocyanates with the hydroxyl groups of polymers (I) and (II) to form pendant *N*-aryluurethane structures. Use of this technique for the preparation of branched polymers held constant other variables which can affect physical properties such as molecular weight and its distribution, polymer backbone structure, distribution of the cure sites, nature of the crosslink, the environment in which the curing system operates, and the fraction of the polymer which is present as loose chain ends at any given state of cure.

These short pendant chains, or branches, were found to have a significant effect upon the rheological and solution properties of the raw polymer and upon the rate of crystallization of the polymer backbone. The basic vulcanizate properties of the polymeric backbone [in polyether urethane (II)], however, were not significantly changed.

The effect of branch concentration on crystallinity was studied by measuring crystallization rates of polymers containing different amounts of phenylurethane branches. For these experiments samples of the polyether urethane (I) were treated with phenyl isocyanate sufficient to react with 50, 75, and 100% of the hydroxyl groups. Half lives for crystallization at 0°C. are shown in Table I. The rate of crystallization was reduced considerably as the number of urethane branches increased. When 100% of the hydroxyl groups were substituted, no crystallization was observed at this temperature.

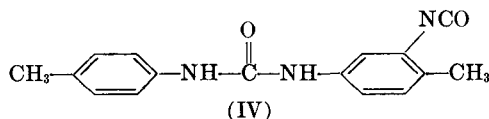
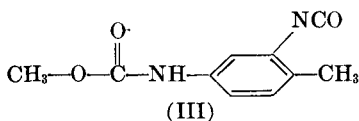
As indicated by the Williams plasticity values, shown in Table I, the polymers became increasingly viscous as the concentration of phenylurethane side chains increased. Recovery values, also shown in

TABLE I
Effect of Branch Concentration on Polymer Properties

Phenylurethane branch concentration, moles/10 ⁴ g.	Half-life of crystallization at 0°C., hr.	Williams plasticity, 30°C.	Williams recovery, 30°C.
0.0	0.7	91	6
4.3	8.8	107	7
6.5	14.8	112	7
8.6	No crystallization	121	9

Table I, were altered only slightly, indicating that the interchain forces—presumably hydrogen bonding—responsible for the viscosity increase decayed relatively rapidly and did not contribute to elastic memory.

The effect of branch structure on physical properties was studied in polymers prepared by reaction of the hydroxyl groups in polyether urethane (II) with phenyl- and α -naphthyl isocyanates, methyl *N*-(3-isocyanato-4-methylphenyl) urethane (III)⁴ and *N*-(3-isocyanato-4-methylphenyl)-*N'*-*p*-tolylurea (IV).



Only 90% of the stoichiometric amount of isocyanate was used. The resulting polymers contained, on the average, one arylurethane branch every 85 atoms along the chain.

Table II shows the effect of different *N*-arylurethane branches on plasticity and recovery. These measurements were made at both 30 and 80°C. At both temperatures, the viscosity of the

polymers increased as the estimated polarity of the aryl branch increased in the order: hydroxyl, monourethane, bisurethane, urethane-urea. At 30°C., the more polar branches, bisurethane and urethane-urea, caused relatively high recovery values as compared to the less polar hydroxyl and monourethane substituents. Thus, the more polar branches introduced interchain forces which persisted for a relatively long time. At 80°C., however, all recovery values were low, indicating a rapid decay of interchain forces. These observations are in accord with the idea that hydrogen bonding is in part, at least, the source of interchain forces in these polymers.

Solution viscosity variations caused by changes in the structure of the side chains are also shown in Table II. The intrinsic viscosities of the branched polymers show little variation with change in structure in the tetrahydrofuran-dimethylformamide solvent. This mixture is a very good one for polar molecules, and hence the viscosities are little affected by changes in the polar nature of the branch. However, in benzene an entirely different situation exists. Intrinsic viscosities of polymers bearing highly polar branches (for example, the bisurethane or the urethane-urea) are lower than is the intrinsic viscosity of the parent polymer bearing hydroxyethyl side chains. This effect can be attributed to coiling of the polar molecules in a poor solvent.

These short chain branches had no major effect on the physical properties of gum vulcanizates measured over a wide range of crosslink density. Figure 1 shows Yezley resilience (25°), 100% modulus and compression set (22 hr./70°C.) as functions of crosslink density (expressed as moles of effective network chains per ml. of polymer). Regardless of the branch structure—whether it be hydroxyl, monourethane, or bisurethane—all the polymers exhibit essentially the same physical

TABLE II
Effect of Branch Structure on Polymer Properties

Structure of branch	Plasticity		Recovery		Intrinsic viscosity at 30°C.	
	30°	80°	30°	80°	THF/DMF	Benzene
—CH ₂ CH ₂ —OH (Control)	90	48	6	0	1.24	1.08
—CH ₂ CH ₂ OC(=O)NHC ₁₀ H ₇	108	53	6	1	1.14	1.17
—CH ₂ CH ₂ OC(=O)NHC ₇ H ₆ NHC(=O)CH ₃	158	69	38	1	1.15	0.90
—CH ₂ CH ₂ OC(=O)NHC ₇ H ₆ NHC(=O)NHC ₇ H ₇	196	91	59	6	1.29	0.60

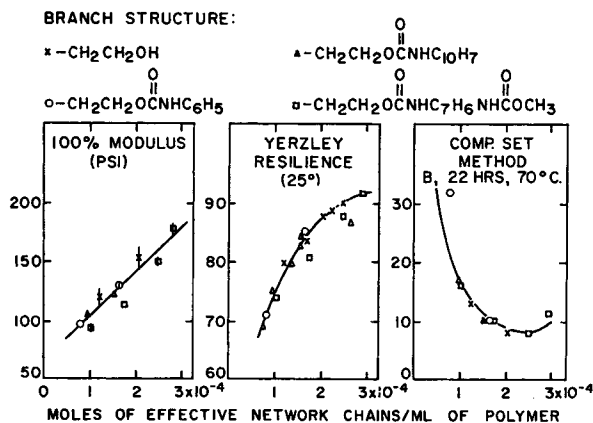


Fig. 1. Dependence of modulus, resilience, and compression set on network chain concentration.

properties at equivalent states of cure. The intermolecular forces responsible for the increase in polymer bulk viscosity and elastic memory in the branched polymers are either not strong enough or are too limited in number to alter significantly these vulcanizate properties.

In agreement with the crystallization rate phenomena observed in derivatives of polyether urethane (I), the temperature retraction measurements recorded in Figure 2 demonstrate that T-50 values of sulfur-cured gum vulcanizates of polymers prepared from polyurethane (II) are greatly lowered by the presence of phenyl- and naphthylurethanoethyl branches. The two polymers with arylurethane side chains have T-50 values about 50°C. lower than that of their parent polymer containing hydroxyethyl branches. The latter crystallizes either to a greater extent or more rapidly when cooled to -60°C., the temperature at which the retraction measurements are started. Retraction

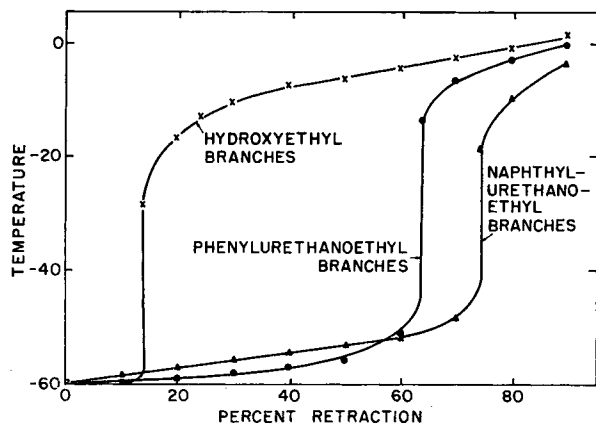


Fig. 2. Dependence of temperature retraction on branch structure.

at low temperatures is limited to the small amount of amorphous material, and the crystalline segments must melt before further retraction can occur. The branched polymers, on the other hand, contain a larger proportion of amorphous material and therefore retract more at low temperatures before reaching the region where crystallinity must disappear for further retraction to occur.

Long Chain Branching

The second phase of this work involved a study of the influence of long chain branching, or "loose-ends," on polymer vulcanizate properties. Here, in contrast to the previous results, long chain branching altered vulcanizate properties significantly.

Condensation of polytetramethyleneether glycol (molecular weight about 1000), trimethylolpropane, and 2,4-hexadiene-1-ol with 2,4-toluenediisocyanate provide branched polymers, the chain-ends of which terminated in a 1,3-diene structure. Network formation (vulcanization) was effected by connecting the terminal diene functions through a Diels-Alder reaction with a bisdieneophile, *m*-phenylenebismaleimide.

This branched chain polyurethane system is unique in that the uncured polymers have cure sites located at every chain end. Reaction of these terminal cure sites with the bismaleimide curative produces the elastic network. Effective network chain concentration is determined by the proportion of trimethylolpropane used in the polymer synthesis and by the number of chain ends connected by the curing agent. For a polymer of given trimethylolpropane content, the concentration of long chain branches in the vulcanizate depends on the amount of bismaleimide curative used.

Figure 3 shows vulcanizate data obtained on one branched chain polyurethane cured with varying amounts of bismaleimide. The polyurethane con-

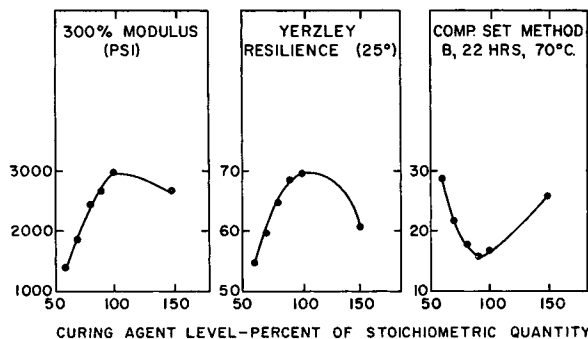


Fig. 3. Dependence of modulus, resilience, and compression set on curative level.

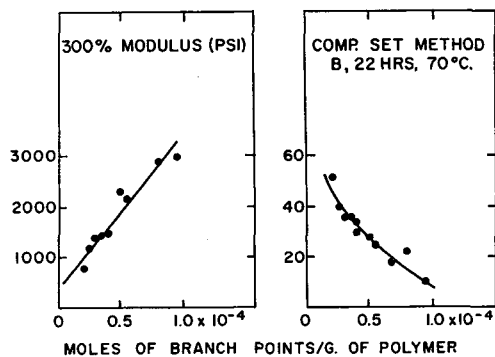


Fig. 4. Dependence of modulus and compression set on branch point concentration.

tained 0.9×10^{-4} moles of branch points, that is, trimethylolpropane per gram of polymer. Modulus at 300% elongation, Yerzley resilience at 25°C., and compression set (22 hr. at 70°C.) have been plotted against the amount of bismaleimide curing agent used, expressed as a percentage of the stoichiometric amount needed to couple all the chain ends. Optimum values of these various vulcanizate properties were attained at close to 100% of the stoichiometric amount of curative.

Modulus displays its expected behavior, on the basis that it is an index of the effective network chain concentration in this system. That is, as the amount of bismaleimide curative is increased—up to a point—more chain ends are connected and, consequently, effective network chain concentration and modulus increase. The maximum in the modulus curve indicates that cure site saturation is occurring in the presence of excess bismaleimide. That this maximum occurs at the theoretical usage of curative is evidence for the highly efficient nature of the Diels-Alder reaction in this system.

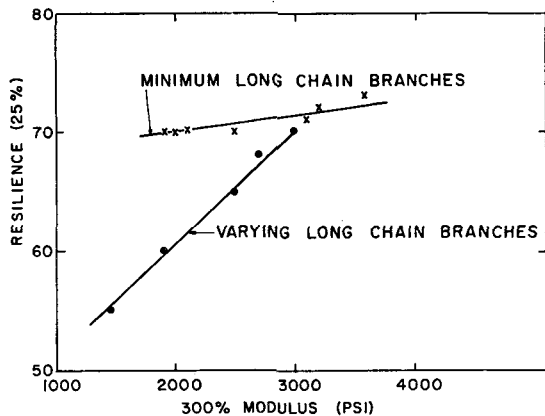


Fig. 5. Dependence of resilience on concentration of long chain branches.

Figure 4 shows the effect of branch point concentration on modulus and compression set. In this series of polymers, effective network chain concentration was varied by changing the concentration of branch points in the raw polymers. All samples were cured with the stoichiometric amount of curing agent which minimized the concentration of "loose ends." Modulus and compression set show the expected variations.

Figure 5 illustrates a significant feature of this polyurethane system. The resilience of vulcanizates in which loose ends are minimized is quite insensitive to the degree of vulcanization. In this graph resilience is plotted against the modulus which here is taken as a measure of the effective network chain concentration. When long chain branch (or "loose end") concentration was minimized by curing with the stoichiometric amount of *m*-phenylenebismaleimide, the resilience changed by only 3 units over a modulus range of 1500 to 3500 psi. In contrast, over this same modulus range in vulcanizates containing long chain branches, the resilience varied by 15 points—from 55 to 70.

CONCLUSION

Attaching short *N*-aryluurethane branches to a high molecular weight, linear polyether urethane introduces interchain forces—very likely arising from hydrogen bonding—which increase as the side chains become more polar. These forces are sufficiently strong to increase the bulk viscosity of the raw polymers and, with the more highly polar groups, are strong enough to impart an appreciable elastic memory. At slightly elevated temperatures (80°C.) these forces are reduced considerably, which is to be expected if they arise through hydrogen bonding. However, they are either not strong enough or are too limited in number to compete with the covalent crosslinks in the elastomer vulcanizates. Thus no significant alteration is observed in the vulcanizate properties which are customarily measured.

The marked effect of these short aryl side chains to reduce crystallization tendencies can most likely be attributed to the bulkiness of the pendant aryl moiety, which prevents—or slows down—the ordering of the polytetramethylene ether chains into a crystal lattice.

Long chain branches influence dynamic properties considerably. Present evidence indicates that optimum dynamic properties—as measured by Yerzley resilience—are obtained when "loose ends" are absent.

References

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Synopsis

The effect of short arylurethane branches on the physical properties of a linear polyurethane is described. Branches of this type reduce crystallization tendencies of the polymer and alter its bulk and solution viscosity behavior. Vulcanizate properties, such as resilience and modulus, are not affected. The synthesis of polyurethanes containing long-chain branches with terminal cure sites is described. Dynamic behavior of these latter polymers, as judged by Yezley resilience, improves as the proportion of long chain branches in the vulcanizate network is reduced.

Résumé

On décrit les effets de courtes chaînes latérales aryluréthaniques sur les propriétés physiques d'un polyuréthane

linéaire. Des chaînons de ce type diminuent les tendances à la cristallisation du polymère et changent la viscosité du polymère en bloc et de sa solution. Les propriétés des vulcanisats, tels leur élasticité et leur module, ne sont pas affectées. On décrit la synthèse de polyuréthanes contenant des longues chaînes latérales se terminant avec des groupes vulcanisables. Les propriétés dynamiques de ces derniers polymères, telles que mesurées par l'élasticité de Yezley s'améliorent quand la proportion de longues chaînes latérales dans le réseau vulcanisé diminue.

Zusammenfassung

Der Einfluss kurzer Arylurethanverzweigungen auf die physikalischen Eigenschaften eines linearen Polyurethans wird beschrieben. Verzweigungen von diesem Typ setzen die Kristallisationstendenz des Polymeren herab und ändern sein Viskositätsverhalten in Substanz und in Lösung. Eigenschaften des Vulkanisates, wie Elastizität und Modul, werden nicht beeinflusst. Die Synthese von Polyurethanen mit Langkettenverzweigungen mit endständigen vulkanisationsfähigen Gruppen wird beschrieben. Das dynamische Verhalten dieser Polymeren wird, nach der Yezley-Elastizität zu urteilen, besser, wenn der Anteil an Langkettenverzweigungen im Vulkanisatnetzwerk herabgesetzt wird.

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