June 15, 1985

Synthesis, Characterization and Properties of Polyisobutylene-Based Polyurethanes

Joseph P. Kennedy, *University of Akron Main Campus*

Synthesis, Characterization and Properties of Polyisobutylene-Based Polyurethanes

JOSEPH P. KENNEDY

Institute of Polymer Science
The University of Akron
Akron, OH 44325

SUMMARY

New rubbery polyurethane networks have been prepared by reacting liquid linear polyisobutylene diols and three-arm star polyisobutylene triols with a triisocyanate and a diisocyanate, respectively. Due to the inherent advantageous combination of properties of the polyisobutylene soft segments, these novel PU networks exhibit excellent high temperature properties, hydrolytic stability, and outstanding barrier characteristics.
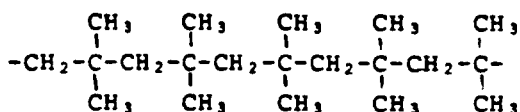
INTRODUCTION

Polyurethane soft segments are conventionally of polyethers or polyesters and for specialty applications may also be of polybutadienes or polysiloxanes. While these polyurethanes exhibit excellent combinations of physical-mechanical-chemical properties, there remains ample room for improvement, more particularly in regard to high temperature, environmental and hydrolytic resistance.

Fundamental polymerization research has recently pointed the way toward a new class of soft segments based on $-CH_2OH$ ended, linear and three-arm star polyisobutylenes. Linear polyisobutylene is a completely saturated heat stable rubbery ($Tg: -73°C$) very low cost ($\sim$25 cents/lb)
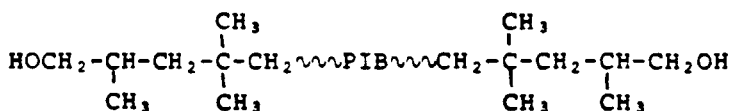
polyhydrocarbon, chiefly used for the manufacture of inner tubes or tubeless tires:

$$-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-$$
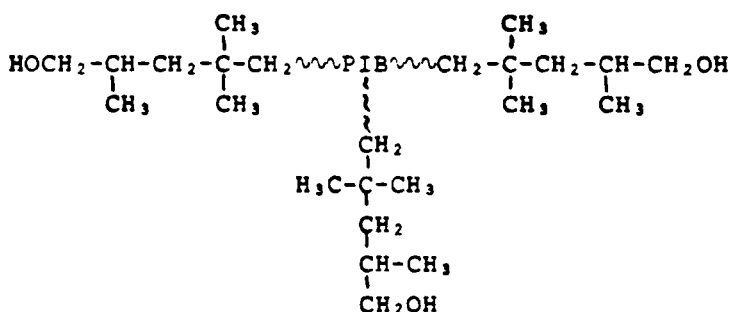
Due to the absence of tertiary hydrogens, the molecule has excellent chemical and environmental (UV) stability. Polyisobutylene exhibits outstanding barrier properties, indeed it is the most important barrier rubber on the market.

Sporadic attempts have been made in the past to prepare polyisobutylenes with primary alcohol ($-CH_2OH$) terminal functions, however, these efforts remained largely unsuccessful. Recently a new polymerization technique, the so called *inifer* technique, has been invented that yielded linear and three-arm star polyisobutylenes PIB's carrying $-CH_2OH$ end groups [1–3]:

$$HOCH_2-\underset{\underset{CH_3}{|}}{\overset{}{C}H}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2\text{vvvPIBvvv}CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{}{C}H}-CH_2OH$$

and

$$HOCH_2-\underset{\underset{CH_3}{|}}{\overset{}{C}H}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2\text{vvvPIBvvv}CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{}{C}H}-CH_2OH$$

$$\begin{array}{c}|\\CH_2\\|\\H_3C-\underset{|}{C}-CH_3\\|\\CH_2\\|\\CH-CH_3\\|\\CH_2OH\end{array}$$

Importantly, the number average terminal functionalities $\overline{F}_n$ of these new materials are exactly 2.0 (for the linear products) and 3.0 (for the three-arm star variety).

The molecular weights of these diols and triols can be controlled by adjusting the polymerization conditions [4,5]. The molecular weight range of greatest interest for polyurethane manufacture is from about $\overline{M}_n = 1000$ to 5000. These materials are colorless, odorless, tasteless, viscous liquids.

For some applications the molecular weight distributions ($\overline{M}_w/\overline{M}_n$) are of great importance. The $\overline{M}_w/\overline{M}_n$ of the linear polyisobutylene is 1.5, and that of the three-arm star variety is 1.33 [6]. These values are determined by the characteristic kinetics of the inifer polymerization mechanism [6].

A great deal of fundamental characterization effort has been directed toward the definition of the above molecular parameters and we are confident that the above very brief description satisfactorily describes the main features of these novel soft segments.

This paper concerns new polyurethane networks that have been prepared by using liquid linear and three-arm star polyisobutylene diols and triols, respectively. Only pure gum-stocks prepared of these alcohols plus isocyanates were examined (absence of extension by 1,4-butenedio or similar extenders), so that the data reflect the fundamental properties of the rubbery networks.

RESULTS AND DISCUSSION

Polyurethane networks have been prepared by the use of PIB-diols plus triisocyanates, and PIB-triols plus diisocyanates [7,8]:
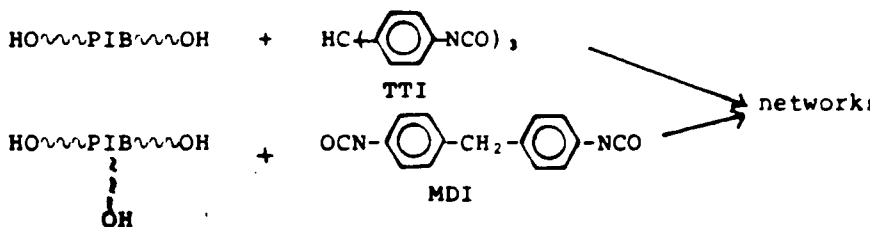
A series of experiments have been carried out with the PIB-triol/MDI networks to demonstrate that the molecular weight between cross-linking points $\overline{M}_c$ is precisely predictable from the $\overline{M}_n$ of the PIB-triol (i.e. $\overline{M}_c = 2 \times \frac{1}{3} \overline{M}_n$). First, networks have been prepared by using a series of PIB-triols having different $\overline{M}_n$'s and demonstrated by extraction measurements that cross-linking was complete (i.e., the amount of extractables was negligible). Then the $\overline{M}_c$ of the networks was determined by two independent methods, e.g., swelling measurements and modulus studies. The data are shown in Table 1. According to the results shown in Table 1, the experimental $\overline{M}_c$'s closely approach the theoretical values which indicate "clean" network formation free from undesirable side-reactions e.g., allophanate formation. This conclusion is also substantiated by the negligible quantities of extractables obtained.

Table 1. Demonstration of model network character of PIB-based polyurethanes.

HO-PIB-OH $\overline{M}_n$	$\overline{M}_c$			Sol Fraction
	Theor.	Exptl.		
		By Swelling[c]	Modulus By Mooney-Rivlin[d]	
3,100[a]	2,066	2,150	2,400	negl.
5,600[a]	3,733	3,500	3,800	negl.
11,600[b]	7,733	8,120	8,400	negl.
21,000[b]	14,000	12,900		negl.

[a] By VPO.
[b] By GPC.
[c] In n-pentane, Flory-Rehner method.
[d] M_c calculated as described in ref. 8.

Subsequently, the effect of hot water and hot air on select mechanical properties (tensile stress, elongation) of a series of "model" networks has been determined by ASTM methods. Thus sheets were prepared and their tensile strengths ($\sigma_{t,b}$) and elongations (E_b) were determined; then they were exposed to hot air (48 hrs. at 128°C) and hot water (96 hrs. at 85°C), cooled to room temperature, and their tensile properties were determined again. Water absorption was also determined. See Experimental for details. Table 2 shows the data. Water absorption (data not shown) was negligible. According to these results the PIB-based networks exhibit very little if any deterioration under the rather severe conditions of the ASTM tests.

Very similar results have also been obtained with linear PIB-diol/TTI systems i.e., very low to negligible loss in tensile properties upon hot water or hot air exposure (by ASTM-D3137 or ASTM-D513, respectively). The water absorption of polyurethane sheets prepared of PIB-diols was also negligible [7].

In view of the very low gas permeability of polyisobutylene-based rubbers (i.e., butyl rubber), it was of interest to determine the gas permeability of polyurethane sheets prepared with PIB-diol soft segments and TTI. Two thin polyurethane films were examined for oxygen gas permeability and the data are shown in Table 3.

For comparison, the permeability coefficient $\bar{P}$ of butyl rubber vulcanizates filled with 50 parts of SRF carbon black is the range of 650–4750 $cm^3 \times mil/(100~in^2 \times 24~h \times atm)$ [10]. Evidently the O_2 permeability of PIB-based PU is much lower than that of butyl rubber. Exact comparisons are difficult to make because it appears that $\bar{P}$ values of unfilled pure butyl gums have not been published.

The very high gas-retention (barrier) property of these novel polyurethanes should be of interest in foam applications. Interesting foams of these materials have been prepared and their cell-structure examined by electron microscopy. Studies in this area are in progress.

EXPERIMENTAL

The preparation of linear and three-arm star PIB diols and triols, respectively has been described [1–5]. Networks were prepared in the dry-box under a nitrogen atmosphere. The PIB-triol/MDI networks were prepared [8] by dissolving the prepolymer in a small amount (>5%) of xylene, adding MDI dissolved in xylene, stirring with a glass rod, and pouring into Teflon molds. The NCO/OH ratio was 1:1. Systems without catalyst were cured for one week at room temperature and for an additional three–seven days at 85°C. Systems with stannous octoate

Table 2. Hot water and hot air resistance of PIB-based polyurethanes.

Sample $\overline{M_c}^{[a]}$	Before Degradation Testing		After Hot Water Exposure[b]		Deterioration %	
	$\sigma_{t,b}$ (Pa)	E_b (%)	$\sigma_{t,b}$ (Pa)	E_b (%)	$\sigma_{t,b}$	E_b
7700	9.4×10^6	510	9.34×10^6	492	negl.	negl.
3700	1.81×10^7	300	1.73×10^7	298	4.4	negl.
2100	1.85×10^7	227	1.76×10^7	222	4.9	negl.
			After Hot Air Aging[c]			
Same as above			9.11×10^6	494	3.1	negl.
			1.76×10^7	290	2.8	negl.
			1.81×10^7	224	2.2	negl.

[a]By swelling in n-pentane.
[b]By ASTM-D3137.
[c]By ASTM-D537.

Table 3. Oxygen permeability of PIB-based PU networks.

HO-PIB-OH M_n	Film Thickness, mil	O_2 Permeability Coefficient, $\bar{P}$* $\dfrac{cm^3 \times mil}{100\ in^2 \times 24\ h \times atm}$
3,400	15	202.5
11,500	20	202

*At 30°C, 89 hr, O_2 purge, 100% humidity.

catalyst were cured for 24 hours at room temperature and for an additional day at 45°C (the catalyst was added with the MDI).

The PIB-diol/TTI networks were made similarly by using THF solvent to facilitate pouring into the mold [7]. Catalyst was not used with these systems. The pads were cured for two weeks at 45° and then for three days under vacuum at 85-90°C.

n-Pentane was used to obtain swelling and extraction data. Preweighed samples were submersed in n-pentane for 24 hrs., blot dried, and weighed. The sample was placed in fresh n-pentane and the procedure repeated until equilibrium weight was reached.

Air oven aging was tested by ASTM-D537. Microdumbbells were suspended in a circulating air oven for 48 hrs. at 128°C, then cooled to ambient temperature for re-testing (Instron). Hydrolytic stability was determined by ASTM-D3137. Samples were suspended in a closed jar containing water for four days at 85°C then cooled to ambient temperature for re-testing. The percent change in tensile properties relative to unexposed samples have been calculated. Water absorption was tested by ASTM-D570. Samples were placed into distilled water at 75°C for two days, then the surface water was blotted off and the samples weighed immediately.

REFERENCES

1. Kennedy, J. P., Smith, R. A., and Ross, L. R., U.S. Patent 4,276,394, June 30, 1981.
2. Kennedy, J. P., U.S. Patent 4,316,973, February 23, 1982.
3. Kennedy, J. P., U.S. Patent 4,342,849, August 3, 1982.
4. Kennedy, J. P. and Smith, R. A., *J. Polym. Sci., Polym. Chem. Ed.*, 18, 1523 (1980).
5. Kennedy, J. P., Ross, L. R., Lackey, J. E., and Nuyken, O., *Polym. Bull.*, 4, 67 (1981).
6. Fehervari, A. and Kennedy, J. P., *J. Macromol. Sci., Chem.*, A15, 215 (1981).
7. Chang, V. S. C. and Kennedy, J. P., *Polym. Bull*, 8, 69 (1982).
8. Kennedy, J. P. and Lackey, J. E., in preparation.
9. Mark, J. E. *Adv. Polym. Sci.*, 44, 1 (1982).
10. *Polysar Butyl Handbook* (1966).