STUDIES LEADING TO IODINE-TAGGED

CROSSLINKED POLYBUTADIENE

Thesis by

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To Tom

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ABSTRACT

Work leading to the synthesis of uniformly crosslinked poly-
butadiene with iodine tags at both ends of a small percentage of the
crosslinking chains is described. The following reactions have been
investigated: conversion of dibromopolybutadiene to diiodopolybuta-
diene; conversion of dihydroxypolybutadiene to polybutadiene diiso-
cyanate; chain extension of polybutadiene diisocyanate with 3-dimethyl-
amino-1,2-propane-diol to form a linear polybutadiene with pendant
dimethylamino groups (PBPA); crosslinking of the PBPA by quaterni-
zation of the amine groups with diiodopolybutadiene; and formation of
the amine salt of PBPA by treatment with hydrochloric acid.

Mechanical properties of PBPA, its HCl salt, and the cross-
linked polybutadiene were determined by free torsional oscillation.
Salt formation apparently leads to pseudo-crosslinking of the polymer
by association of the ionic groups, so that the polymer exhibits
elastomeric behavior between -30° and 40°C. Crosslinking of PBPA
by quaternization of the amine groups with diiodopolybutadiene extends
the elastic region to 130°C, where creep begins due to degradation of
the polymer.

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I. SYNTHESIS

A. Introduction

One of the long-disputed questions in the field of polymer science is whether the mean-square distance between crosslink points in a polymer network is the same as the mean square end-to-end distance for a free chain having the same contour length. In developing their statistical theories of rubber elasticity, Kuhn[1], Wall[2], and Flory[3] made the assumption that the distribution of chain vector lengths in the unstrained network is identical with the instantaneous distribution of chain vector lengths for a corresponding set of free chains. James and Guth[4] contended that this assumption was unrealistic and developed their theory using a different approach. The results obtained from the two methods for the modulus of the network are quite similar; James and Guth predict modulus values lower by one half. However, for lack of any experimental evidence, the assumption that the mean-square distance between crosslink points in a network is identical with the mean square end-to-end distance for a corresponding set of free chains has become generally accepted.

Until recently, the methods of determining polymer dimensions have been limited to solution techniques, namely light scattering[6] and intrinsic viscosity[7], and therefore to soluble linear polymers. However, a new method for investigating the dimensions of bulk polymers by small-angle x-ray scattering has recently been developed[8]. This method was used to determine the end-to-end distance of linear polystyrene in a cast film. It involved tagging both ends of 5% of the

polymer molecules with silver ions through the silver salt of a carboxylic acid. These small-angle x-ray studies seemed to indicate that molecular dimensions in bulk polymers are somewhat larger than those of the unperturbed chain, i.e. the dimensions of the polymer in a theta-solvent.

Small-angle x-ray scattering thus provides the necessary means of measuring directly the distance between crosslink points in a polymer network. All that is required is a polymer network with heavy atom tags at both ends of a small percentage of the chains. (Each segment of a network between successive crosslink points is known as a "chain".) Tagging all crosslink points would lead to too much interference in the x-ray pattern and would not reveal which pair of heavy atoms was attached to the same chain. In order for the results to be meaningful, the average contour distance between tags should be the same as the average contour length in the network. For the x-ray studies it is desirable to have a narrow distribution of these distances; a wide distribution leads to a strongly concave scattering curve which makes the determination of the mean-square end-to-end distance difficult.[9] If a suitable material could be synthesized, it could also be used in a low-angle x-ray study of the effect of strain and temperature on the mean-square length of the chains of the network. The aim of the first part of this study was the synthesis of such a network. Although this goal has not yet been achieved, the feasibility of such a synthesis has been shown. In working toward this goal, several other interesting polymers have been synthesized and their mechanical properties investigated.

B. Proposed Reaction Scheme

Because a rubbery network is desired for the x-ray studies, polybutadiene is the material of choice for the major portion of the elastomer. In order to simulate a soft-gum vulcanizate, the chain between crosslink points should have a molecular weight of approximately 5000. Hydroxyl terminated polybutadiene (HTPB) is commercially available as a prepolymer with a molecular weight 5000 and with a functionality of 1.8. The commercial material is prepared by anionic polymerization, and therefore should have a narrow molecular weight distribution.

Our plan was to react the HTPB with a diisocyanate to form an isocyanate-terminated polybutadiene. This could then be crosslinked by reaction with a triol to obtain a network with fairly uniform spacing between crosslink points (see Fig. 1). The crosslinking reaction would have to be done in bulk, because if a solvent were used and then removed after crosslinking, a supercoiled polymer would result. (Supercoiling of the chains may have some effect on the mechanical properties as well as the distribution of chain end-to-end distances.)

This reaction scheme would then be modified (as explained below) to allow introduction of iodine atoms at both ends of a small percentage of the network chains. Rather than using a stoichiometric amount of triol in the above reaction, a small percentage of crosslinks would be formed by an amine diol and diiodopolybutadiene. The amine diol would link two isocyanate-terminated chains; a crosslink would then be provided by quaternization of amine groups of two different part of the network by diiodopolybutadiene of molecular weight 5000. This is shown in Fig. 2.

$$CH_3-CH-CH_2-(CH_2-CH=CH-CH_2)_n-CH_2-CH \underset{HO}{\overset{CH_3}{\diagdown}}OH + 2 \, OCN-(CH_2)_6-NCO \quad (or \; OCN-\langle\text{benzene}\rangle-CH_3 \, with \, NCO)$$

$$OCN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{CH}}-CH_2-(CH_2-CH=CH-CH_2)_n-CH_2-\overset{CH_3}{\overset{|}{CH}}-O-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NCO$$

$$\downarrow \; ^{2}/_{3} \; HO-CH_2-\overset{CH_2CH_3}{\underset{CH_2OH}{\overset{|}{C}}}-CH_2OH$$

Figure 1

• = urethane linkage

▬ = isocyanate residue
$[-(CH_2)_6-$ or $-\langle\text{benzene}\rangle-CH_3]$

$\curlywedge$ = triol residue $[-CH_2-CH-CH_2-$ with $\overset{CH_2}{\underset{CH_2CH_3}{|}}]$

$\sim\!\!\sim$ = polybutadiene, M.w. ~5000

$OCN-(CH_2)_6-NH-\overset{O}{\overset{||}{C}}-O-CH-CH_2-(CH_2-CH=CH-CH_2)_n-CH_2-\overset{CH_3}{\underset{|}{CH}}-O-\overset{O}{\overset{||}{C}}-NH-(CH_2)_6-NCO$

$+ \quad HO-CH_2-\overset{CH_2OH}{\underset{|}{C}}-CH_2-CH_3$

$+ \quad HO-CH_2-\overset{CH_2OH}{\underset{|}{\underset{CH_2-N}{\overset{|}{CH}}}}-OH \overset{CH_3}{\underset{CH_3}{}} \quad + \quad I-(CH_2-CH=CH-CH_2)_n-I$

$\longrightarrow$

• = urethane linkage

$\overline{-N-}$ = amine diol residue

⋀ = triol residue

wwww = polybutadiene, MW ~5000

= isocyanate residue $[-(CH_2)_6$ or $\bigcirc-CH_3]$

triol residue $\left[-CH_2-\overset{CH_2}{\underset{CH_2}{\overset{|}{CH}}}-CH_2CH_3\right]$

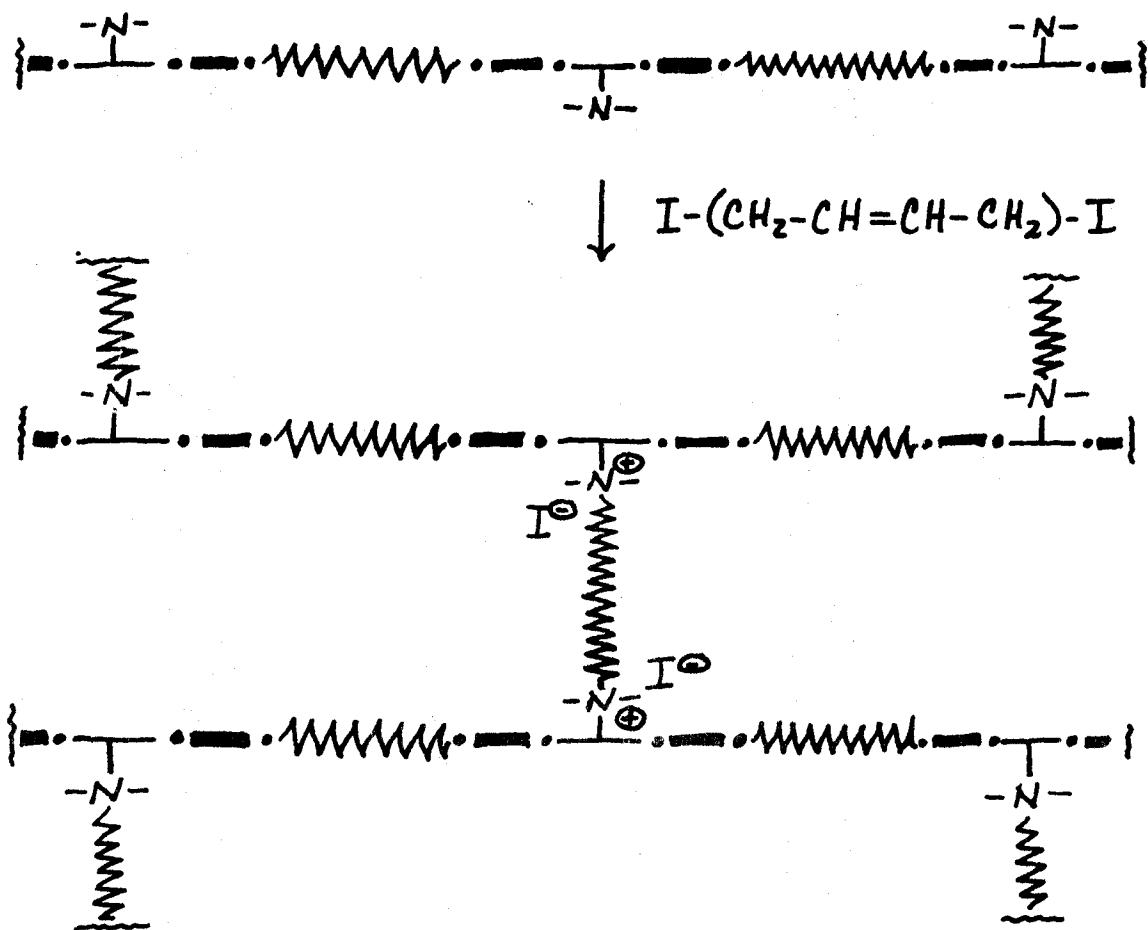Figure 2

C. Experimental Studies

Because the above synthesis of the elastomer involves a rather complex reaction mixture, it was desirable to first investigate separately (1) the reaction of polybutadiene diisocyanate with trimethylol propane to form a crosslinked network, (2) the reaction of polybutadiene diisocyanate with 3-dimethylamino-1,2-propanediol to form a linear, chain extended polymer, and (3) the subsequent crosslinking of this material with diiodopolybutadiene. (See Fig. 3). A study was made of points (2) and (3). Time did not permit dealing with point (1).

Synthetic work was carried out in four major areas: (1) conversion of dibromopolybutadiene to diiodopolybutadiene; (2) formation of polybutadiene diisocyanate from dihydroxypolybutadiene; (3) chain extension of polybutadiene diisocyanate with 3-dimethylamino-1,2-propanediol; and (4) quaternization of the linear chain-extended polybutadiene with diiodopolybutadiene to form a crosslinked network. A discussion of the results of this work and the problems encountered is given below.

Details of the materials, synthesis and analysis procedures will be found in the Appendix. Mechanical properties of some of these compounds were also investigated, and this work is described in Part II of this paper.

1. Diiodopolybutadiene (DIPB)

Dibromopolybutadiene was chosen as the starting material because of its commercial availability in molecular weights suitable for our purposes. Alkyl bromides are usually converted to alkyl iodides by refluxing with an excess of sodium iodide in acetone or methyl ethyl ketone.[10] Unfortunately, polybutadiene is not soluble in either of these solvents and the best solvent which could be found for

$$OCN{-}{\blacksquare\hspace{-0.3em}\cdot}\text{WWWWWW}\cdot{\hspace{-0.3em}\blacksquare}{-}NCO \quad + \quad HO-CH_2-CH-OH$$

$$CH_2$$

$$CH_3-N-CH_3$$

$$\downarrow$$

$$\{{\blacksquare}\cdot\overset{-N-}{|}\cdot{\blacksquare}\cdot\text{WWWW}\cdot{\blacksquare}\cdot\underset{-N-}{|}\cdot{\blacksquare}\cdot\text{WWWW}\cdot{\blacksquare}\cdot\overset{-N-}{|}\cdot{\blacksquare}\}$$

$$\downarrow \quad I-(CH_2-CH=CH-CH_2)-I$$

Figure structure with polybutadiene chains, amine diol residues, $I^{\ominus}$ ions, and $-N^{\oplus}-$ groups

- • = urethane linkage
- ▬ = isocyanate residue
- WWW = polybutadiene
- -N- = amine diol residue

Figure 3

both the polymer and sodium iodide was tetrahydrofuran. The reaction was carried out on polymers of molecular weights 5000 and 3500.

Infrared absorption spectra of dibromopolybutadiene and the product of the above reaction were identical except for one absorption peak which may be attributed to $-CH_2X$ (CH_2 wagging)[11]. This absorption appeared at 1205 cm^{-1} for the dibromo compound and at 1150 cm^{-1} for the diiodopolybutadiene. (Assignment of these absorptions was confirmed by comparison with the spectra of allyl bromide and allyl iodide.) The 1205 cm^{-1} absorption was nearly absent from the spectrum of the diiodo compound. This seems to indicate a high degree of reaction conversion.

A sample of diiodopolybutadiene (prepared from dibromopoly-butadiene of molecular weight 3500) was analyzed for bromine and iodine. For 100% conversion of the bromide to the iodide, the analysis result should be 7.05% I and 0% Br; however, the sample contained 3.78% I and 2.50% Br as determined by Spang Microanalytical Labs. These analysis results seem to indicate only 48% conversion of the bromide to the iodide. Some of the discrepancy in the results could be due to incomplete removal of inorganic salts from the polymer before analysis, in spite of several careful washings. However, as the calculated molecular weight, based on the analysis results and two halogen atoms per chain, is 3200, and the stated molecular weight is 3500, sodium bromide should not be responsible for more than about 20% of the analysis result for percent bromine.

Incomplete reaction could be due to two factors: low solubility of sodium iodide in tetrahydrofuran, and steric hindrance to conversion

of any secondary bromide to iodide. To check the importance of the
second factor, an estimate of the relative amounts of primary and
secondary bromide in the dibromopolybutadiene was desired. The
relative amounts of 1,4- and 1,2-butadiene addition in the polymer
should give a fairly accurate estimate of the relative amounts of primary
and secondary bromide, respectively, assuming that the ratio of 1,2-
to 1,4-addition is the same for the chain ends as for the bulk of the
polymer. The relative amounts of 1,4- and 1,2-addition can easily
be determined by analysis of the nuclear magnetic resonance spectrum
of the polymer.[12] On this basis about 20% of the bromide in the mole-
cule is secondary. Therefore, steric hindrance could be a major cause
of incomplete conversion of the bromide to the iodide.

Perhaps a better method of preparing diiodopolybutadiene would
be from the HTPB which is to be used as the basis for the rest of the
network. By reaction with methanesulfonyl chloride or p-toluene-
sulfonyl chloride in pyridine, the HTPB could be converted to the
dimesylate or ditosylate,which should react quantitatively with sodium
iodide to give the desired diiodopolybutadiene, since the mesylate and
tosylate functions are far more reactive than bromide. This is shown
in Fig. 4.

This reaction scheme would provide the additional advantage
that all of the polybutadiene chains in the final crosslinked network
would have the same microstructure. The relative amount of 1,2- and
1,4-addition in polybutadiene determines the glass transition temperature
(T_g) of the polymer, and the commercially available dihydroxypoly-
butadiene and dibromopolybutadiene have different microstructures
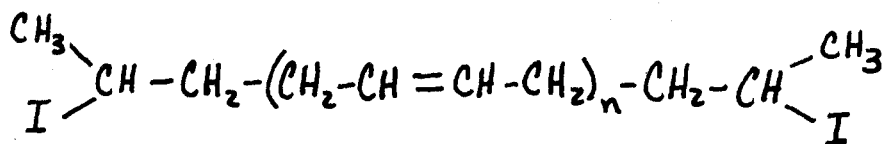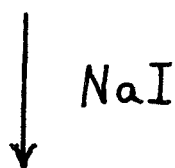
$$\underset{HO}{\overset{CH_3}{\diagdown}}CH-CH_2-(CH_2-CH=CH-CH_2)_n-CH_2-CH\overset{CH_3}{\underset{OH}{\diagup}}$$

$$RSO_2Cl \quad\Big|\quad \Big(R= CH_3- \text{ or } CH_3-\!\!\langle\!\!\langle\;\rangle\!\!\rangle\!\!-\Big)$$

$$\underset{RSO_2O}{\overset{CH_3}{\diagdown}}CH-CH_2-(CH_2-CH=CH-CH_2)_n-CH_2-CH\overset{CH_3}{\underset{OSO_2R}{\diagup}}$$

$$\Big|\; NaI$$

$$\underset{I}{\overset{CH_3}{\diagdown}}CH-CH_2-(CH_2-CH=CH-CH_2)_n-CH_2-CH\overset{CH_3}{\underset{I}{\diagup}}$$
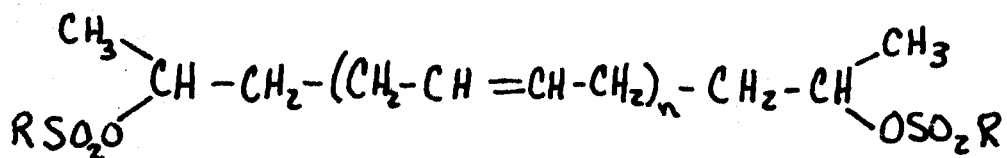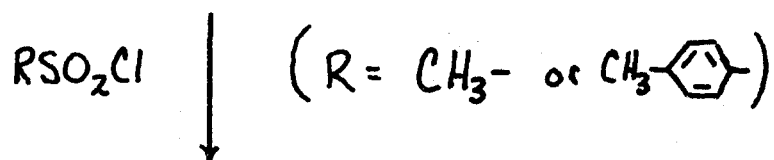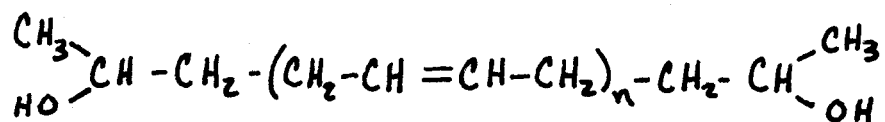
Figure 4

with different T_g's. The incorporation of diiodopolybutadiene having

a certain microstructure in a network having a different microstructure

would significantly alter the T_g of the network.

2. Polybutadiene Diisocyanate

The reaction of hydroxyl terminated polybutadiene with hexa-

methylene diisocyanate was investigated in order to determine suitable

reaction conditions for the formation of a diisocyanate-capped polymer.

The reaction of an alcohol with an isocyanate may be followed convenient-

ly by the disappearance of the −OH absorption in the infrared at 2.8μ.

Because this absorption is quite weak for HTPB of $\overline{M}_n = 5000$, the

reaction was first undertaken with HTPB of lower molecular weight

(and therefore stronger hydroxyl absorption). The IR spectrum showed

no −OH absorption after 45 hours reaction.

The reaction of the higher molecular weight material was

carried out under similar reaction conditions. This time, however,

an excess of diisocyanate and a longer reaction time were used to

insure complete reaction. To remove the excess diiosocyanate before

reaction with a diol or triol, the polymer was precipitated in dry

acetone.

Because exact equivalents of isocyanate and hydroxyl are

necessary for a high degree of polymerization in the crosslinking

reaction, it was desirable to analyze the polymer for isocyanate

content. The procedure used was essentially that of Burkus and

Eckert.[13] The polymer was reacted with an excess of n-butylamine

in dioxane and the unreacted amine determined by back-titration with

a standard $HClO_4$ solution in dioxane using methyl red as indicator.

The isocyanate content determined by this procedure was 0.69%. The hydroxyl content of the polymer was given by the supplier, Phillips Petroleum Company, as 0.60%. Based on this figure, a polymer of 1.40% NCO should have been obtained. The procedure for isocyanate determination was checked using hexamethylene diisocyanate and a result approximately 8% low was obtained. However this result is not low enough to explain the anomalously low isocyanate content observed in the polybutadiene diisocyanate produced above.

In order to determine if the hydroxyl content of the HTPB was indeed 0.60% as stated by Phillips, their analysis procedure was repeated. The polymer was acetylated by treatment with acetic anhydride in pyridine using perchloric acid as catalyst. The excess acetic anhydride was hydrolyzed and the hydroxyl content of the polymer was determined by the difference between blank and sample titrations with sodium hydroxide using a mixed cresol red-thymol blue indicator. A great deal of difficulty in determining the true end-point was encountered, as the indicator color faded rapidly. The use of excess pyridine to solublize the polymer was helpful, but did not solve the problem completely. The hydroxyl content was determined as 0.5% rather than 0.6%. A combination of this result and a low result from the isocyanate determination would explain an isocyanate content only as low as 1.16%.

The low isocyanate content was therefore attributed 1) to chain extension of the HTPB by a coupling reaction with hexamethylene diisocyanate or 2) to destruction of some of the isocyanate by reaction with water. Therefore, the reaction of HTPB with hexamethylene

diisocyanate was repeated 1) using twice the required amount of hexa-methylene diisocyanate to favor formation of the end-capped rather than chain extended polymer, and 2) using reagents and solvents which were carefully dried before reaction and maintaining an atmosphere of dry nitrogen throughout the reaction and precipitation. The polymer was dried and analyzed for isocyanate, this time using the procedure of DuPont, which seemed much more satisfactory than the previously used procedure of Burkus and Eckert.

The sample was reacted with an excess of di-n-butylamine in toluene. After addition of a large volume of isopropyl alcohol, the excess amine was titrated potentiometrically with standard hydrochloric acid. The isocyanate content was determined as 0.72% which agrees well with the determined isocyanate content of the previously prepared polymer (0.69%). Therefore, anhydrous reaction conditions, a large excess of hexamethylene diisocyanate, and an atmosphere of nitrogen did not seem to have any effect on increasing the isocyanate content of the polymer. An isocyanate content of 0.72% for polybutadiene diisocyanate of molecular weight 5300 corresponds to a functionality of only 0.9 -NCO groups per molecule. Therefore this material is not suitable for preparing a crosslinked network if the analysis results are valid.

Whether the cause of the low isocyanate content is the HTPB, incomplete reaction of hexamethylene diisocyanate with the HTPB, or faulty analysis procedures has not been conclusively shown. One explanation for the contradictory results could be basic impurities in the HTPB, which may have arisen in its preparation by anionic polymer-

ization. These basic impurities would lead to erroneously high results for hydroxyl content and erroneously low results for isocyanate content, as determined by the acid-base titration procedures used. This should be checked before proceeding with work on this material.

All further work preparing an isocyanate-capped polybutadiene was carried out using HTPB of lower molecular weight obtained from General Tire Corporation. Because the lower molecular weight poly-butadiene diisocyanate could not be precipitated by acetone, it was used without isolation or analysis in the succeeding reactions discussed below.

3. Polybutadiene with Pendant Dimethylamino Groups (PBPA)

Polybutadiene with pendant dimethylamino groups was made by reacting HTPB with a diisocyanate to form the isocyanate end-capped polymer, which was not isolated but rather further reacted with 3-dimethylamino-1, 2-propanediol to form the chain extended PBPA. The amine function acts as a catalyst in the latter reaction. Complete reaction was achieved after 24 hours in benzene solution at $55^{\circ}C$, as shown by the complete disappearance of the isocyanate peak at 4. 4 μ in the infrared spectrum. The polymer can be isolated by precipitation in methanol.

HTPB from General Tire Corporation was available with functionalities of about 2. 4 and 1. 5 with equivalent weights of 1282 and 1100 respectively. Much difficulty was encountered in attempts to use the material of higher functionality. The reaction mixture formed an insoluble gel after reaction with the amine diol; this was not unexpected, because a functionality greater than 2 theoretically can lead to chain branching and eventually to crosslinking. Because an HTPB function-

ality of 1.5 imposes a strong limitation on the molecular weight of the chain extended polymer, a functionality greater than 1.5 (but less than or equal to 2) was desired. Therefore the two HTPB polymers were mixed to obtain an average functionality of 1.96. The isocyanate-capping and chain-extension reactions were carried out as before on this mixture, but again the reaction mixture gelled.

Attempts to form a high molecular weight polymer by use of the material of functionality 1.5 were in general unsuccessful. The molecular weight of the best polymer obtained (PBPA-4) was only 12,500 ± 300 (as determined by membrane osmometry on solutions of the polymer in toluene), even when nearly exact equivalents of isocyanate and alcohol functions were used.

Two methods for the determination of the equivalent weight per dimethylamino group of the chain-extended polymer were tried. One method involved treatment of the polymer with a known amount of HCl in tetrahydrofuran and determination of the excess HCl by potentiometric titration with standard barium hydroxide solution. This was a modification of the procedure of Akagi and co-workers[14]. Much difficulty with precipitation of the polymer near the end point was encountered and the equivalent weight per dimethylamino group was determined as 2890, which is about 10% higher than expected (2670).

A second method for the determination of the equivalent weight of the polymer involved treatment of the polymer with excess HCl in tetrahydrofuran and removal of the solvent and excess HCl under vacuum. The sample was then analyzed for chloride. Based on the 1.38% chloride content found (Elek Microanalytical Lab.), the molecular weight per dimethylamino group can be calculated as 2544.

Polybutadiene is very sensitive to air oxidation because of the unreacted double bonds. Therefore, it is very important that an antioxidant be added to the polymer before storing. A phenolic antioxidant, 2,2'-thiobis-(4-methyl-6-t-butyl)phenol was used. A sample of the linear chain extended polymer without antioxidant had crosslinked through air oxidation after 4 months at room temperature, as shown by the fact that the polymer was no longer soluble in benzene or tetrahydrofuran and swelled only to a small extent in these solvents.

4. Crosslinked Polybutadiene with Halogen Tags at All
   Crosslink Points

The reaction of linear α, ω-diamines $(R_2N(CH_2)_xNR_2)$ and linear α, ω-dihalides $(Br(CH_2)_yBr)$ in polar solvents at moderate temperatures has been used by Rembaum and co-workers[15] to synthesize polymers with positively charged atoms in the polymeric backbone (ionenes). The same type of reaction was also used to prepare various crosslinked polymer networks[16]. Suitable prepolymers terminated with dimethylamino groups were mixed in benzene solution with prepolymers terminated with bromine, and the resulting mixtures were cast in Teflon molds.

Crosslinking of the PBPA sample described in Section 3 (equivalent weight $\sim$ 2670) was carried out in a similar manner by mixing the polymer with dibromo- or diiodopolybutadiene ($\overline{M}_n \approx 3500$) at room temperature in benzene or tetrahydrofuran (THF), and allowing the solvent to evaporate in a mold. That the resulting polymer is indeed crosslinked is indicated by the fact that it swells but does not dissolve in benzene or THF; in addition its mechanical properties are typical of an elastomer, as discussed in Part II.

Obtaining a film suitable for mechanical property studies was difficult. When cast from 10% solution in tetrahydrofuran, the polymer when dry had shrunk to approximately 1/3 the size of the mold. The sample was nonuniform in thickness, having a depression in the center. Benzene is not as good a solvent for the PBPA as THF, and should swell the polymer less. Therefore, the mixture of DIPB and PBPA was next cast from 14% solution in benzene. However, some shrinking still occurred. This indicates that crosslinking is taking place before the solvent has completely evaporated from the polymer. Casting from more concentrated solution should alleviate the shrinkage problem to some extent. However, a supercoiled polymer will be obtained unless some method can be found of mixing the two prepolymers without using solvent. Although diiodopolybutadiene is a viscous liquid, the DBPA is a viscoelastic solid, and mixing without a solvent would be difficult to accomplish.

D. Suggestions for Further Studies

The successes in obtaining a linear polybutadiene with pendant dimethylamino groups by an isocyanate reaction and in crosslinking this material with a dihalopolybutadiene are good indications of the feasibility of the proposed reaction scheme for the synthesis of a polymer with iodine tags at both ends of a small percentage of the crosslink points. The main areas still to be investigated are 1) cross-linking of the isocyanate-terminated polybutadiene with a triol, and 2) reaction of the isocyanate-terminated polybutadiene with a mixture of triol, amine diol, and diiodopolybutadiene. Two other areas need further investigation, namely obtaining diiodopolybutadiene with higher

iodine content, and obtaining an isocyanate-capped polybutadiene with

a functionality close to 2.

## II. MECHANICAL PROPERTIES

A. Introduction

The effect of charge on the mechanical properties of polymers has recently become an area of great interest. (An excellent review of the physical properties of ionic polymers is given by Otocka[17]). Several types of ionomers have been investigated. One way of making polymers with pendant ionic groups begins with the copolymerization of vinyl monomers containing acidic or basic groups (e.g. methacrylic acid or 2-methyl-5-vinylpyridine) with other monomers such as butadiene or styrene. The functional group is later converted to its salt form, leading to an ionomer with the charge randomly distributed along the chain. Both monovalent and divalent salts have been made, but only monovalent salts will be discussed here. Formation of the monovalent salt frequently increases the glass transition temperature, T_g, of the polymer, although this is not true for all salts. For example, the tetraethyl quaternary ammonium salt of a methacrylic acid-stryene copolymer has a lower T_g than the acid form of the same copolymer.[18]

In an extensive study on the lithium salts of butadiene-methacrylic acid copolymers by Otocka and Eirich[19] a quasi-rubbery region in plots of modulus versus temperature was observed. In this region, the tensile modulus increased with the square of the salt-group content, indicating some sort of dimer association between the salt groups[19]. In similar investigations by the same workers on the methyl iodide quaternizates of butadiene/2-methyl-5-vinylpyridine copolymers, two distinct transition regions were observed, in between which the polymers behaved as if they were covalently crosslinked.

Elastomeric behavior of ionomers between two transition regions has also been observed with a totally different type of ionomer by Dieterich and co-workers[20]. A polyether diol ($\overline{M}_n \sim 2000$) which had been reacted with an excess of hexamethylene diisocyanate to form the polyester diisocyanate, was further chain extended with N-methyl-imino-2, 2'-diethanol to give a polymer with tertiary nitrogens in the backbone. These nitrogens were quaternized by reaction with methyl iodide or dimethylsulfate to give an ionomer which had a decreased T_g and showed elastomeric behavior between -30° and 120°C. Treatment of the polymer with hydrochloric acid gave an ionomer having the same properties as the quaternized products. The mechanism postulated to explain the elastomeric behavior in this case is alignment of the polymer chains by the ionic groups to permit increased hydrogen bonding, as well as coulombic interaction between charged groups. (Fig. 5).

An investigation of the effect of positive charge on the mechanical properties of PBPA (polybutadiene with pendant dimethylamino groups, as described in Part I) was undertaken in an attempt to further elucidate the mechanism of quasi-crosslinking of polymer networks by ionic groups. Positive charge was introduced into the polymer by treating it with HCl to form the amine salt (PBPA-HCl). A further comparison of the mechanical properties of PBPA treated with HCl and of PBPA chemically crosslinked by quaternization of the amine groups with DIPB was made.

Although Rembaum and co-workers[16] have determined plots of modulus versus temperature for polymers crosslinked by the reaction of amines with dihalides, a comparison of the effect of
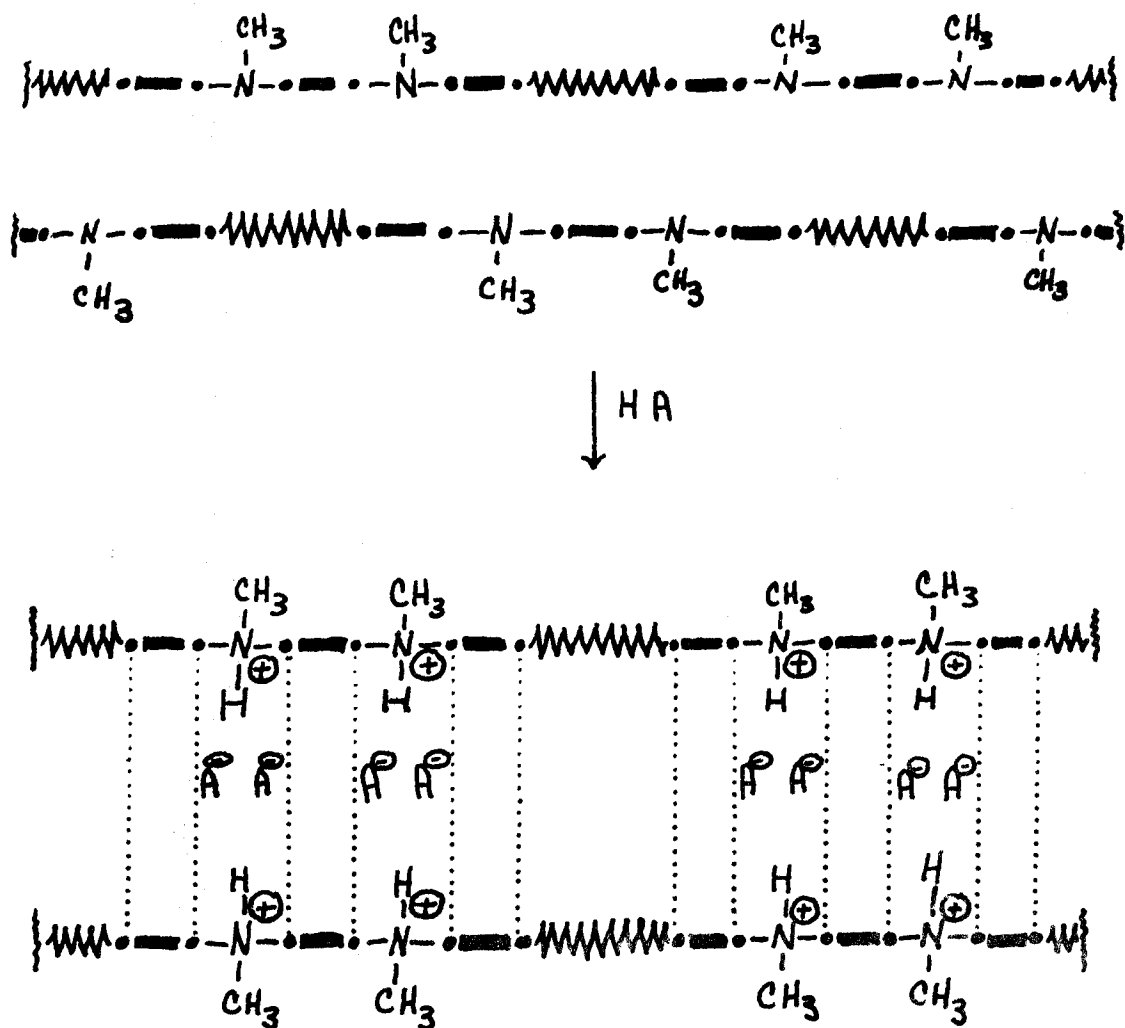
• = urethane linkage   ▬ = isocyanate residue

ᗯᗯ = polyester   .... = hydrogen bond

Figure 5

chemical crosslinking of this type with the pseudo-crosslinking effect

of the association of charged groups has never been made before. The

only related investigation was made by Dieterich and co-workers[20],

who found that the rubbery modulus of a linear polymer pseudo-cross-

linked by the association of charged groups was reduced by chemical

crosslinking of the polymer through urea linkages.

B. Materials and Methods

The preparation of films of PBPA, its amine salt (PBPA-HCl),

and a crosslinked network from PBPA and DIPB are described in the

appendix. Dynamic mechanical measurements were made on a recording

torsion pendulum[21]. A Hall device was used to provide the voltage

source for measurement. With this device measurements were made

at deflections of about 1^O. Samples used were approximately 5 cm X

1 cm X 0.2 cm, and strains were less than 2%.

C. Results and Discussion

Plots of the dynamic storage modulus (G') and loss tangent

(tan δ) versus temperature for the three samples are shown in Figs.

6 and 7. The maximum in the plot of tan δ vs. T gives an estimate of

the T_g of the polymer. The temperature of the maximum loss of PBPA

(-40^OC) is lowered by formation of the hydrochloride salt of the amine

to -45^OC. That of the chemically crosslinked polymer (PBCR), -55^OC,

is even lower, due primarily to the incorporation of the DIPB in the

network, which has a larger percentage of 1,4-butadiene addition (hence

lower T_g) than the polybutadiene of the PBPA.

Figure 6. Plot of the Logarithm of the Storage Modulus vs. Temperature for PBPA, PBPA-HCl, and PBPA Crosslinked with DIPB(PBCR).
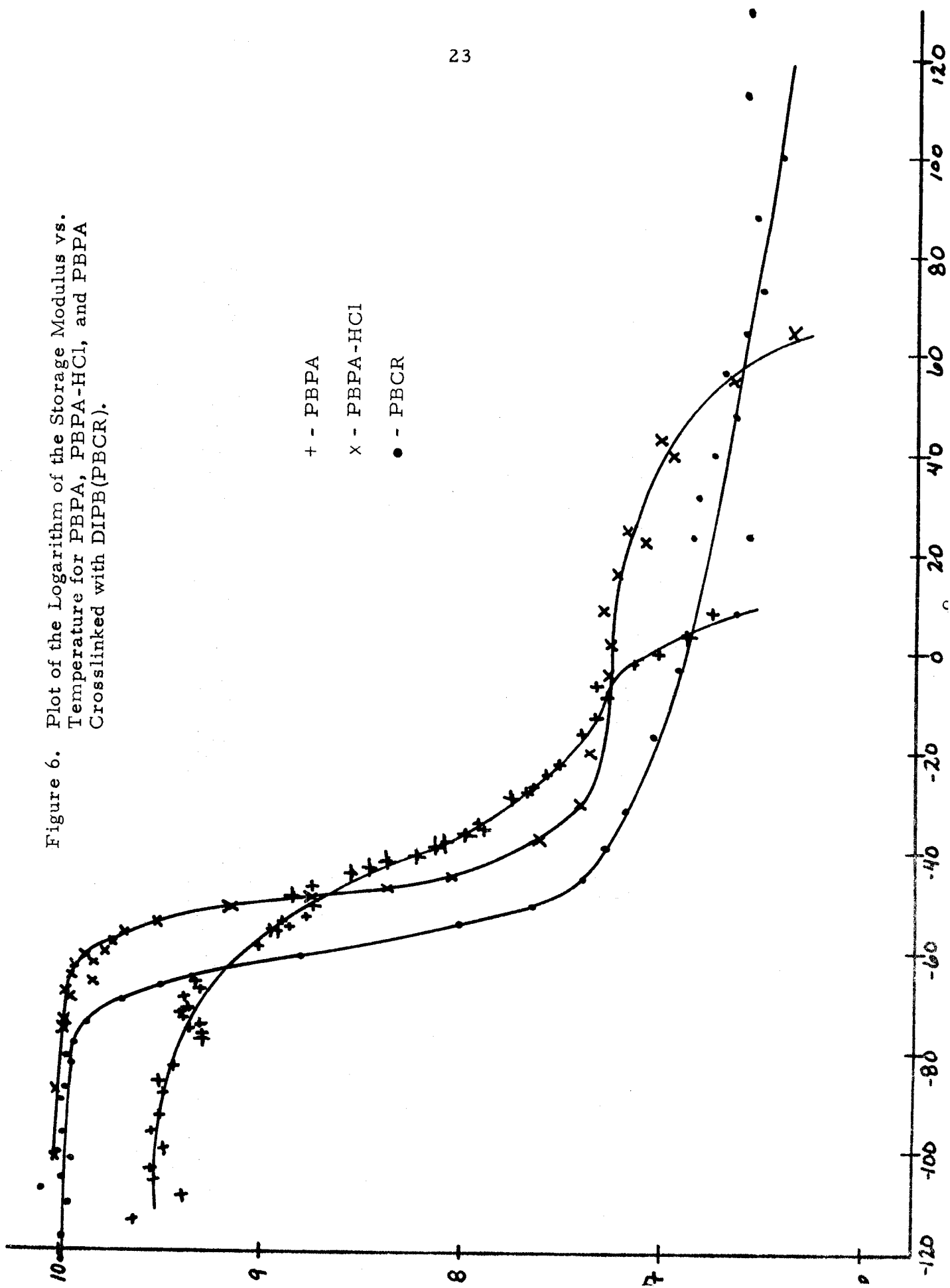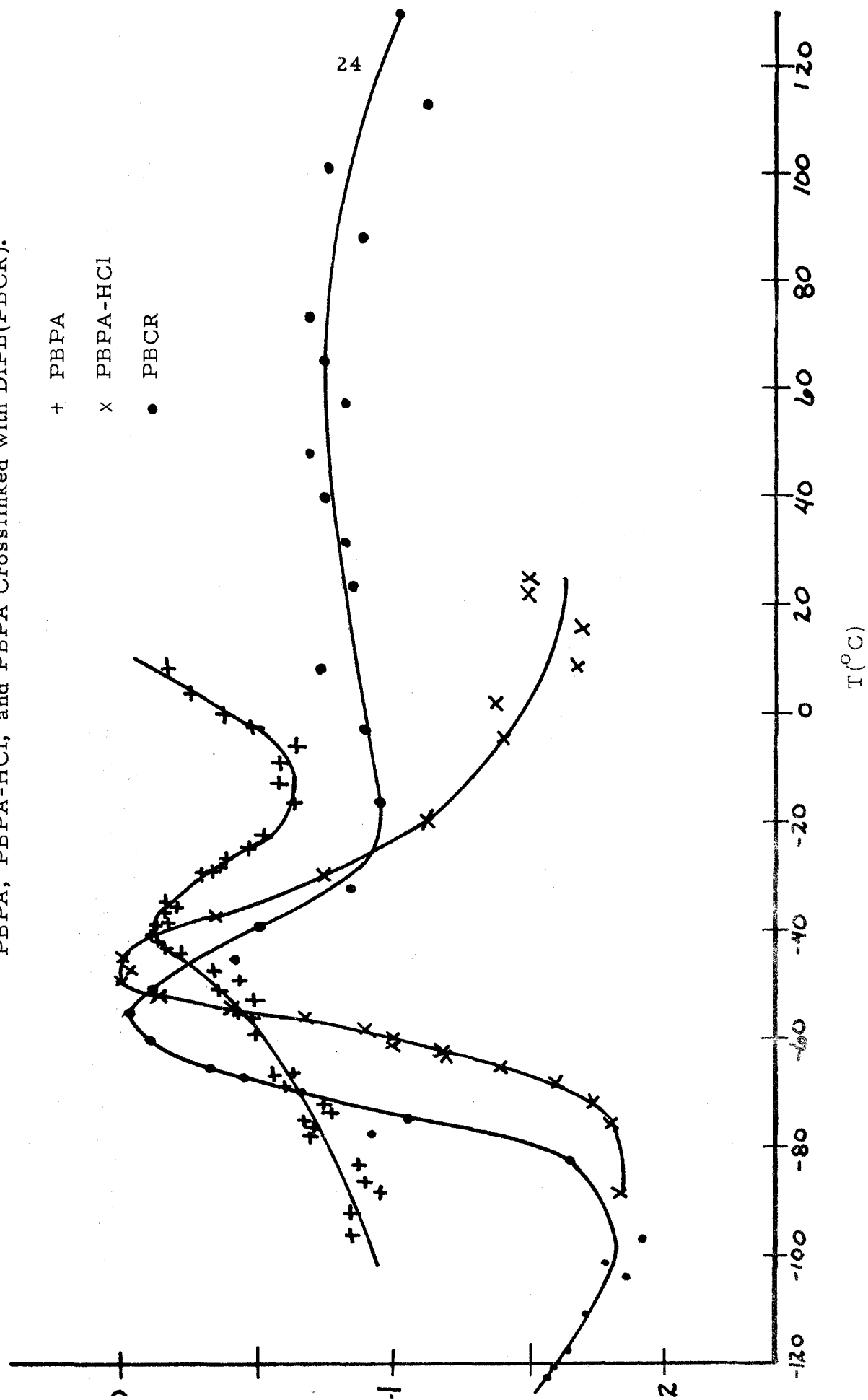
+ - PBPA

x - PBPA-HCl

• - PBCR

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Figure 7. Plot of the Logarithm of the Loss Tangent vs. Temperature for PBPA, PBPA-HCl, and PBPA Crosslinked with DIPB(PBCR).

+ PBPA

× PBPA-HCl

• PBCR

$T(^{\circ}C)$

In Fig. 6, the glassy modulus of PBPA-4 ($10^{9 \cdot 6}$ dynes/cm^2) is lower than that of the two other samples (10^{10} dynes/cm^2). A short entanglement plateau is observed for this sample around -10°C; the modulus falls off rapidly with temperature above -5°C.

That the ionic groups of PBPA-HCl (charge content 3.64×10^{-4} equivalents/g) indeed associate to form pseudo-crosslinks is evident when plots of G$'$ vs. T for PBPA and its hydrochloride salt are compared. A rubbery plateau between -30°C and 40°C is observed for the PBPA-HCl. At the higher temperature these associations evidently become labile. This behavior is quite similar to that exhibited by the methyl-(2-methyl-5-vinyl)-pyridinium iodide copolymer of similar charge content (3.05×10^{-4} equivalents/g) of Otocka et. al.[19] However, the polymer does not show elastomeric behavior over the large temperature range observed by Dieterich and co-workers[20] for similar ionomers based on polyesters and containing nitrogen atoms in the backbone. This could be due to the fact that hydrogen bonding between urethane functions of the type shown in Fig. 5 is sterically less likely for the PBPA-HCl in which nitrogen atoms are two atoms removed from rather than part of the polymer chain containing the urethane linkages.

A much broader temperature range of elastomeric behavior is observed for the PBPA crosslinked with DIPB (PBCR). The rubbery plateau extends from -40°C to 130°C. Creep began above 130°C. Within 20 minutes after increasing the temperature to 150°C the sample had flowed considerably. Since both polybutadiene and polyurethanes are stable at 150°, degradation was probably located at the quaternary

nitrogens forming the crosslinkages. Hofmann elimination is a plausible mechanism of degradation. (See Fig. 8). Because these linkages are stable up to 130°, iodine-tagging of a polybutadiene by the proposed method should lead to a network suitable for any desired mechanical property studies.

PBCR, when cooled after heating to above 150^OC, is again an elastomer. This fact might make similar polymers candidates for injection moldable rubbers, and warrants further investigation.
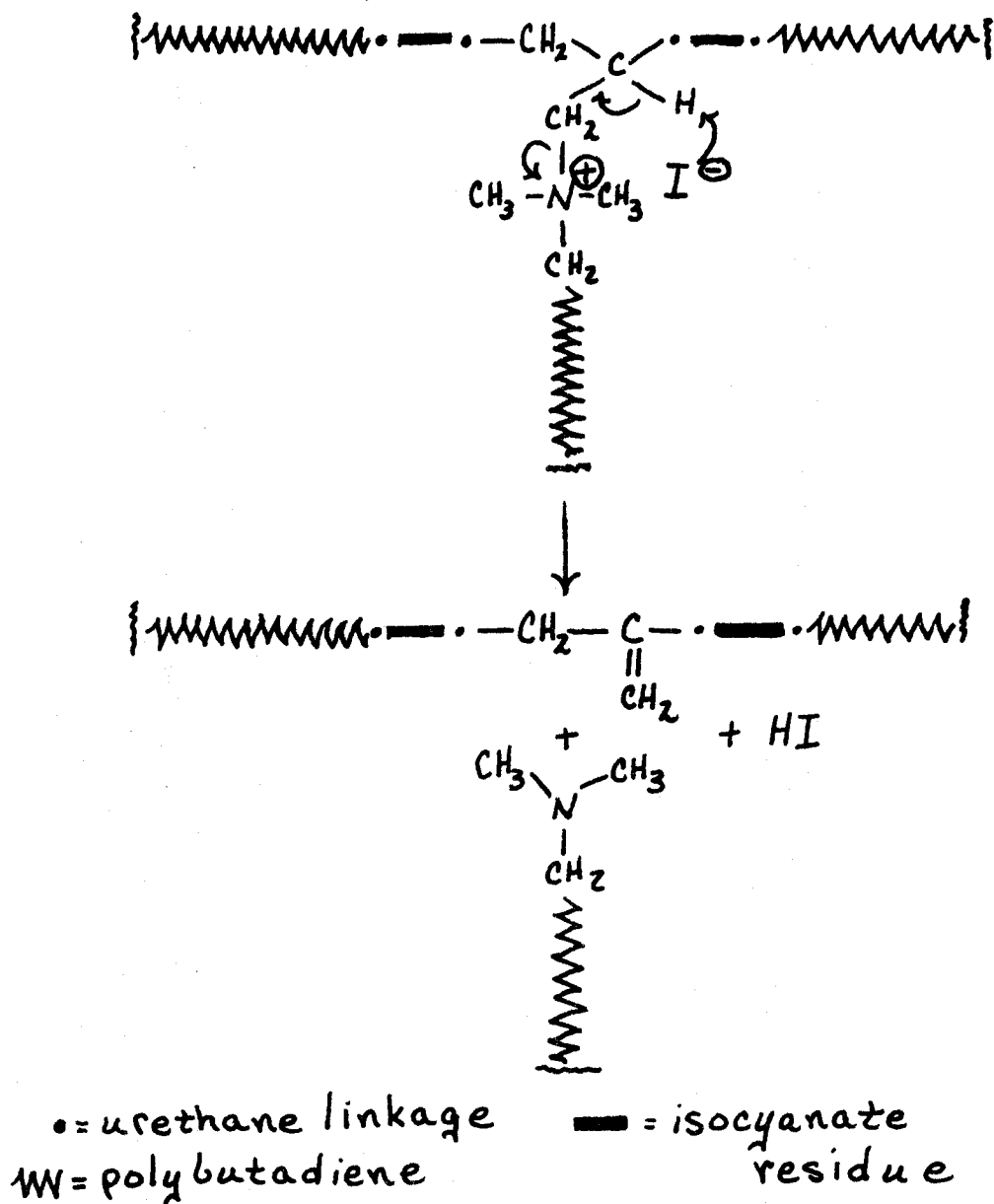
Degradation of Polymer Network
by Hofmann Elimination

• = urethane linkage   ▬ = isocyanate
ᗯ = polybutadiene   residue

Figure 8

APPENDIX

Instrumentation

Infrared spectra were taken with a Perkin-Elmer 257 Grating Infrared Spectrophotometer.   NMR spectra were taken with a Varian Associates A-60-A Analytical NMR Spectrometer.

A.   Diiodopolybutadiene

Materials

Dibromopolybutadiene (Polymer Corp. Limited, $\overline{M}_n$ = 5000 and 3500) was purified by stirring three times with an excess of acetone decanting and then drying under vacuum.   The NMR spectrum indicates about 20% 1,2-addition and 80% 1,4-addition of the butadiene in the polymer.

Sodium iodide was dried at 120° for 48 hours.

Tetrahydrofuran was dried over lithium aluminum hydride and distilled under nitrogen.

Reagent grade methanol was used.

Procedure

20 g. (0.133 mole) sodium iodide was refluxed in 300 ml. tetrahydrofuran to dissolve as much of the salt as possible.   To this was added 50 g. (0.0143 mole) dibromopolybutadiene ($\overline{M}_n$ = 3500).   The mixture was then refluxed for 22 hours under dry nitrogen.   The reaction mixture was cooled and the polymer was precipitated by pouring slowly with stirring into 1 liter methanol.   In order to remove inorganic salts, the polymer was redissolved in 200 ml. benzene and reprecipitated with 500 ml. methanol.   This was repeated, and the polymer was stirred with a further 300 ml. portion of methanol.   The

polymer was then stirred with two 200 ml. portions of acetone to remove any traces of sodium iodide. After decanting 0.40 g of 2,2'-thiobis-(4-methyl-6-t-butyl) phenol antioxidant (CAO-4) was added and the polymer dried under vacuum. The reaction of the 5000 molecular weight material was carried out in an essentially similar manner. Samples sent for analysis were further washed four times with dry acetone and dried under vacuum.

B. Polybutadiene Diisocyanate I

Materials

Hydroxyl terminated polybutadiene (Butarez HT) was obtained from Phillips Petroleum Company with $\overline{M}_n$ = 5000 and −OH content = 0.60%.

Hydroxyl terminated polybutadiene (Telagen HT) was obtained from General Tire Corporation with an equivalent weight of 1282 and functionality = 2.4.

Hexamethylene diisocyanate was obtained from Matheson, Coleman and Bell.

Benzene (reag. grade) was dried over molecular sieves.

Acetone (reag. grade) was dried over molecular sieves.

Procedure

In order to determine reaction conditions, 64.1 g (0.05 equivalents) HTPB (eq. wt. 1282) was reacted with 8.41 g (0.05 moles) hexamethylene diisocyanate in 200 ml. benzene at 65°C. The reaction was followed by the disappearance of the −OH absorption in the IR spectrum at 2.8μ. The reaction was complete after 45 hrs.

85 g. (0.03 equivalents) HTPB ($\overline{M}_n$ = 5000) in 120 ml. benzene was added to 5.56 g. (0.033 moles) hexamethylene diisocyanate in 30 ml. benzene. The mixture, protected by a drying tube, was heated at 65°C for 4 days. The polymer was precipitated by pouring into 1 l. acetone. The polymer was allowed to settle overnight after which the acetone was decanted and the polymer dried at 45°C and 20 mm. pressure for 24 hours.

The IR spectrum of the polymer showed a strong isocyanate absorption at 4.4μ. The polymer was stored in a sealed flask under N_2 in a refrigerator.

Isocyanate content was determined as 0.69% by the method of Burkus and Eckert[13] except that n-butylamine was used in this test rather than di-n-butylamine.

C.   Polybutadiene Diisocyanate II

Materials

Hydroxyl terminated polybutadiene (Butarez HT, Phillips Petroleum, $\overline{M}_n$ = 5000, OH content = 0.6%) was dried for 18 hours at 55°C and 20 mm.

Hexamethylene diisocyanate was distilled (b.p. 64-68°C at 0.07 - 0.08 mm. pressure).

Benzene (reag. grade) was dried over calcium hydride and distilled.

Acetone (spectral grade) was dried by filtering through a column of molecular sieves.

Procedure

The reaction was carried out under dry nitrogen. 85.0 g. (0.03 equivalents) HTPB in 120 ml. dry benzene was added slowly with stirring to 9.8 ml. (0.06 moles) hexamethylene diisocyanate in 30 ml. benzene. The solution was heated at 65°C for 4 days. The polymer was precipitated by pouring into 750 ml. acetone within a dry bag filled with nitrogen. After decanting, the polymer was stirred with another 350 ml. portion of acetone to remove any excess hexamethylene diisocyanate. The polymer was stored in a sealed flask under N_2 in the freezer.

Analysis for isocyanate was carried out by the procedure of DuPont, which is given below. The isocyanate content of the polymer was determined as 0.72%.

Analysis for hydroxyl content of the HTPB was carried out using the procedure of Phillips Petroleum which is also given below. The hydroxyl content was determined as 0.50%.

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

ELASTOMER CHEMICALS DEPARTMENT

WILMINGTON, DELAWARE 19898

ISOCYANATE

Dibutylamine Method, Potentiometric Titration in Toluene

I. Scope and Application

This method is applicable to the determination of isocyanate groups in liquid urethane polymers. The method is applicable to the determination of -NCO in the range of 0 to 30.0%.

II. Principle

The sample in a toluene solution is reacted with an excess of di-n-butylamine. The excess di-n-butylamine is then titrated potentiometrically with standard hydrochloric acid.

III. Interferences

Acidic or basic materials of any nature will interfere. Water must be carefully excluded from the reagents up to the point of the addition of the isopropyl alcohol.

IV. Sensitivity, Precision, and Accuracy

No statistical study has been made of the reproducibility of this method. Duplicate results by the same technician should be considered suspect if they differ by more than 0.06%.

V. Apparatus

1. Lowy pipet, 50 ml

2. pH meter, Beckman model G (or equivalent) with glass and calomel electrodes

3. Magnetic stirring apparatus

VI. Reagents

1. Di-n-butylamine in toluene, 0.1 N
   Add 17 ml di-n-butylamine to 1 liter dried toluene. The toluene should be prepared as follows:

   a. Remove and discard the first 10-20% of the solvent by distillation through a 15 in. Vigreaux column (or equivalent).

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b. Pass the cooled pot residue through a 2 in. od glass column 24 in. long packed with 1/16 in. pellets of Molecular Sieve, Type 4A. Use newly-purchased Molecular Sieve and discard the column contents after the passage of about 20 liters of toluene.

c. Discard the first 10% of each run through the column and collect the remainder in the dried receiver in which it is to be stored.

2. Hydrochloric acid, 0.1 N, standard

3. Toluene, purified
The toluene should be prepared as covered in item 1, above.

4. Isopropyl alcohol

VII. Sampling

Avoid transferring the sample in the presence of high humidity.

VIII. Safety Precautions

1. Toluene and isopropyl alcohol are flammable. Keep sparks and flames away.

2. The samples may contain free HYLENE® T. HYLENE T may cause local irritation of the skin and care must be taken to avoid unnecessary contact. Do not inhale vapors of the sample.

IX. Procedure

1. Add 50 ml (grad cyl) of toluene to a clean dry 400 ml beaker.

2. Weigh a sample of suitable size into the toluene in the beaker.

NCO Range	Sample Size
0 – 5%	2.0 – 3.5 g
5 – 8%	1.3 – 2.0 g
8 – 10%	1.0 – 1.3 g
10 – 15%	0.7 – 1.0 g
15 – 20%	0.5 – 0.7 g
20 – 30%	0.3 – 0.5 g

3. Cover beaker with a watch glass. Stir the sample in the toluene for 20 min. Inspect the solution carefully to be certain the sample is completely dissolved.

4. Add 50.00 ml (Lowy pipet) of 0.1 N di-n-butylamine solution (Note 2).

5. Cover beaker with a watch glass and stir for an additional 5 min.

6. Add exactly 200 ml (grad cyl) isopropyl alcohol, using part of the alcohol to wash off the underside of the watch glass.

7. Stir for 2 min.

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8. Assemble the pH meter with glass vs. calomel electrodes. Switch to pH range on the meter and standardize the instrument with pH 4 buffer solution.

9. Immerse the electrodes in the sample solution and titrate with 0.1 N standard HCl to the break. The equivalence point will occur at a pH of about 5.50. Titrate using small exact incremental additions (0.1 ml) near the end point.

10. Run blanks in exactly the same manner as the sample except omitting the sample and the 20 min stirring time (Note 2).

11. Determine the equivalence point of the titration.

12. Run duplicates on the blanks and on the sample.

X. Calculations

$$\% -NCO = \frac{(B - A) \times N \times 4.202}{S}$$

Where A = vol HCl for sample, ml

B = vol HCl for blank, ml

N = normality of HCl solution

S = wt sample, g

XI. Notes

1. Use the Lowy pipet in the following manner: after filling the pipet, wipe off the outside of the tip with clean cheesecloth. When adding the contents of the pipet to the beaker, hold the tip of the pipet against the side of the beaker. After the fast flow has stopped, continue to hold the tip against the side of the beaker for exactly 15 sec to allow it to drain.

2. Pipet the 0.1 N di-n-butylamine solution for the blanks and the sample determinations within 15 min, in order to minimize volume variations caused by temperature change.

XII. References

1. ASTM Proposed Tentative Methods for Chemical Analysis of Urethane Foam Raw Materials D-1638.

Origin: Elastomers Area Laboratory
              Chambers Works

Prepared by: M. H. Horner

Approved by: W. C. Percival
              G. S. Cook

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DETERMINATION OF HYDROXYL GROUPS IN POLYMERS
BY PERCHLORIC ACID CATALYZED METHOD

[Adopted from method of J. S. Fitz and G. H. Schenk, Anal. Chem. 31, 1808(1959)]

SUMMARY

Hydroxyl groups in polymers are determined by acetylation in pyridine solution using perchloric acid to catalyze the reaction. The amount of hydroxyl present is calculated from the difference between the blank and sample titrations with sodium hydroxide.

REAGENTS AND SOLUTIONS

2M Acetic Anhydride in Pyridine. Cautiously add 1 ml. of 72% perchloric acid dropwise to 30 ml. of reagent grade pyridine* in a 125-ml. glass stoppered flask. Pipette 10 ml. of acetic anhydride into the flask with magnetic stirring. Because this reagent discolors and decreases in anhydride content after a few hours, it should be prepared fresh daily.

0.55M Sodium Hydroxide. To 33g sodium hydroxide dissolved in 154 ml. boiled water, add 1350 ml. of absolute methanol. Filter NaOH solution and standardize against standard HCl solution using cresol red-thymol blue mixed indicator.

Mixed Indicator. Mix 1 part 0.1% neutralized aqueous cresol red with 3 parts 0.1% neutralized thymol blue.

PROCEDURE

Weigh approximately 3 g. of polymer into 125-ml. glass stoppered flasks and pipette into it exactly 3 ml. of 2M acetic anhydride in pyridine. Shake flasks on a mechanical shaker for 1 hour. Add 5 ml. pyridine to each flask and continue shaking for one additional hour.** A reagent blank is determined at the same time by an identical procedure excluding the polymer sample.

The excess acetic anhydride is next hydrolyzed. One ml. of water is added to each flask and the mixtures shaken 5 minutes, then 10 ml. of 3 to 1 pyridine-water solution is added and the flasks allowed to stand for 5 minutes. For most polymers the addition of 50 ml. additional pyridine before titration has proved helpful.

Titrate samples and blank with 0.55M sodium hydroxide using the mixed indicator, and take the change from yellow to violet as the end point. Titrate dark-colored samples to an apparent pH of 9.8 using glass-calomel electrodes and a pH motor. Use the difference between the blank, V_b, and the sample titration, V_s, to calculate the percentage of hydroxyl compound in the polymer.

CALCULATION

$$\text{Wt. \% OH} = \frac{(V_b - V_s) \times N_{NaOH} \times 0.017 \times 100}{\text{Sample Wt. (grams)}}$$

NOTES:

 * Keep drying agent in pyridine before using. Avoid water during reaction step.

** 1/2 hr. reaction time after sample is dissolved is sufficient.

D. Polybutadiene with Pendant Dimethylamino Groups (PBPA)

Materials

Hydroxy-terminated polybutadiene (Telagen, General Tire Corporation, (eq. wt. 1100, functionality 1.5) was dried at $100^{o}C$ for 3 hours at 1 mm. The NMR spectrum of the polymer indicates about 50% 1,2-addition and 50% 1,4-addition of the butadiene in the polymer.

Benzene was distilled from calcium hydride.

2,4-tolylene diisocyanate (TDI) was used as obtained from the Jet Propulsion Laboratory, Polymer Research Section.

3-dimethylamino-1,2-propanediol (Eastman) was distilled through an 18 cm. Vigreaux column b.p. 41-$43^{o}C$ at 0.05 - 0.07 mm.

Reaction Conditions

The reaction was carried out under dry nitrogen. 88.0 g. (0.080 equivalents) HTPB in 135 ml. benzene was added over 30 mins. with an addition funnel to 14.04 g. (0.0806 moles) TDI in 35 ml. benzene. After 15 hours at $62^{o}C$, the $-OH$ absorption in the IR spectrum at 2.8μ had disappeared. 4.77 g. (0.0400 moles) 3-dimethylamino-1,2-propanediol in 35 ml. benzene was then added and heating was continued for 20 hours until the $-NCO$ absorption in the IR at 4.4μ had disappeared. 1.5 g. CAO-4 antioxidant in 60 ml. benzene was added to the polymer before precipitation of the polymer in 1 l. methanol. To quench any unreacted isocyanate, the polymer was allowed to stand in methanol for 5 hours before decanting and drying. The polymer (PBPA-4) was stored in the freezer.

The chain extension reaction using 3-dimethylamino-1,2-propanediol was also carried out under similar reaction conditions using isocyanate-terminated polybutadiene which had been prepared from HTPB of functionalities 1.5, 2.4, and 1.96 (obtained from a mixture of the two) using a 5-10% excess of hexamethylene diisocyanate. The polymer from HTPB of functionality 1.5 (PBPA-1) was quite tacky even after the removal of solvents. The reaction mixture gelled with the higher functionalities. These products were not used in mechanical property studies.

Osmometry

A sample of PBPA-4 for osmometry was purified by dissolving 2 g. in 30 ml. reag. benzene, filtering the solution, and precipitating with 90 ml. methanol. The sample was dried under vacuum for 24 hours. The osmotic pressure (π) of solutions of the polymer in toluene (reag. grade) of concentrations ranging from 1 to 10 g. per liter was determined with a Melabs Membrane Osmometer at 40°C, and the number average molecular weight of the polymer was found from the intercept of a plot of π/c vs. c as 12,500 $\pm$ 300. [$\overline{M}_n = RT/(\pi/c)_{c=0}$].

Films

Films of PBPA-4 approximately 1 mm. thick were cast from 10% solution in THF (which had been distilled from $LiAlH_4$ to destroy peroxides). 0.5% CAO-4 antioxidant was added to the polymer solution before casting. Drying under vacuum had to be done very carefully by gradually reducing the pressure to avoid bubble formation in the sample.

E. Crosslinking of PBPA with DIPB

Materials

The preparation of DIPB ($\overline{M}_n$ = 3200) and PBPA have been described above. THF was treated with $LiAlH_4$ to remove peroxides and distilled.

Reagent grade benzene was used.

Procedure

2.54 g (0.00159 equivalents) of DIPB was added with stirring to a filtered solution of 4.22 g. (0.00158 equivalents) PBPA-4 in 45 ml. benzene containing 0.02 g. CAO-4 antioxidant. The solution was degassed by a freeze-thaw cycle and cast in an 8 x 10 cm. Teflon mold. This sample (PBCR) was used for torsion pendulum measurements. The sample shrank to $6\frac{1}{2}$ x 6 cm. when dry. A film cast from THF solution had greater shrinkage. The polymer swells but does not dissolve in benzene of THF. A crosslinked polymer was also prepared using dibromopolybutadiene in place of DIPB and casting from benzene.

F. Amine Salt of PBPA

Materials

PBPA-1 and PBPA-4 were prepared as described above.

Tetrahydrofuran (THF) was treated with $LiAlH_4$ to remove peroxides and distilled under nitrogen.

Reagent grade methanol was used.

Reagent grade hydrochloric acid (38%, DuPont) and hydriodic acid (51.7%, Baker) were used. The hydriodic acid also contained 1.52% H_3PO_4 as preservative.

Procedure

In the first attempt to prepare the HCl salt of PBPA, 24 g

dried PBPA-1 (0.009 equivalents) was dissolved in 100 ml THF and

filtered. 0.85 ml conc. HCl (0.01 equivalents) was added dropwise to

this solution, which was stirred magnetically. After 20 min. stirring,

400 ml abs. MeOH was added in an attempt to precipitate the polymer

and remove the excess HCl Only about 5 g of the polymer precipitated;

the rest became emulsified, and the emulsion was stable to centrifugation

at 9000 rpm for 1 hour. However, the addition of 5 ml saturated NaCl

solution caused immediate precipitation of the polymer due to its

polyelectrolyte-character (salting-out effect). (PBPA not treated with

acid precipitates from THF solution immediately upon the addition of

methanol. Chloride analysis of the polymer salt precipitated without

NaCl gave 0.95% Cl; the polymer precipitated by NaCl contains 1.50%

Cl. (Spang Microanalytical Lab.) As the theoretical chloride content

for this polymer is 1.32% Cl, it was concluded that not all the amine

groups reacted, and that NaCl was not completely removed by the water

washing.

In order to obtain a better chloride sample for mechanical

property studies, 8.0 g (0.003 equivalents) PBPA-4 was dissolved in

80 ml THF containing 0.04 g CAO-4 antioxidant. 0.5 ml (0.006

equivalents) conc. HCl was added dropwise and the solution stirred for

4 hours at room temperature. THF was removed under aspirator

pressure and the polymer (PBPA-HCl) placed under vacuum at 0.02 mm

for 24 hours to remove the excess HCl. A sample sent for analysis

was dried an additional 48 hours. Chloride analysis gave 1.38% Cl

(Spang Microanalytical Lab.) (Theoretical is 1.32% Cl.)

To obtain a film for torsion pendulum studies PBPA-HCl was dissolved in 80 ml THF and the solution filtered, degassed, and cast in a 7 x 6.2 cm Teflon-lined mold.

To form the iodide salt of PBPA-4 11.8 g (0.0044 equivalents) PBPA-4 was dissolved in 100 ml THF containing 0.06 g CAO-4 anti-oxidant and treated with 1.47 ml conc. HI. After stirring for 4 hours at room temperature, the polymer (PBPA-HI) was dried as above. Iodine analysis gave 6.13% I. (Spang Microanalytical Lab.). (Theoretical is 4.54%; apparently all the HI was not removed under vacuum. Some addition to double bonds could have occurred). A film was cast from solution in 100 ml THF in an 8 x 8 cm Teflon mold. The polymer turned reddish-brown during the casting process, probably because of oxidation of the excess iodide ions.

Formation of the amine salt of PBPA-4 noticeably altered the character of the material. The parent compound is tacky and deforms easily when handled; the amine salt is not tacky and keeps its shape.

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