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Synthesis and Properties of a New Class of Potential Biomedical Polymers*

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SUMMARY

Both low molecular weight compounds and some polyelectrolytes containing quaternary nitrogen atoms in their structure have been known for some time to possess important biological activity. Aliphatic ammonium compounds are used as bacteriocides and muscle relaxants, and quinolinium compounds have recently been found to be excellent antileukemic agents. In addition, a considerable amount of evidence has been accumulated to show that organic ammonium salts combine with heparin, and the resulting complex may be used as a coating to render polymers blood-compatible. However, the introduction of ammonium groups into the backbone of a polymer exhibiting good mechanical properties offers certain advantages.

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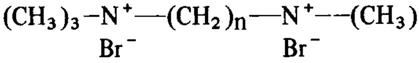
The present paper describes a synthesis of a new family of polymeric elastomers containing quaternary nitrogen atoms in the polymeric backbone. They may be prepared from the following commercially available materials: (A) polyhydroxy prepolymers reacted with diisocyanates first and then with dimethylamino alcohols, (B) tetramethyl or hexamethylamino alkanes and α,ω-dibromoalkanes, and (C) halo prepolymers formed from diisocyanates reacted with halo alcohols. It is thus possible to obtain a very large numer of homo or block elastomers with a variable concentration of positive charges as well as of hydrophilic and hydrophobic segments by A-B, B-C, and C-A reactions.

One of the block polymers obtained from Solithane 113 and dibromopolybutadiene was examined in detail. Heparin was grafted onto its surface by a simple impregnation treatment, and the resulting material was found to be antithrombogenic. Electron scanning micrographs show that the surface structure of the elastomer was altered by heparinization. Thermograms from a Perkin-Elmer scanning calorimeter exhibited two transitions: one around -80°C, being identified as the glass transition temperature of the polybutadiene blocks, and another very broad transition near room temperature due to the Solithane blocks. Modulus-temperature and modulus-time curves determined by viscoeleastic measurements show only the low temperature transition. There is a continuous decrease in modulus with increasing temperature and time above the polybutadiene T_g. It was demonstrated from the WLF plot that the free volume fraction in this range is smaller than in ordinary homopolymers. Above 100°C the modulus drops, indicating the onset of interchange reactions of the polyurethane linkages. Fracture tests of the heparinized and unheparinized polymers indicate that these elastomers have good tensile strength properties.

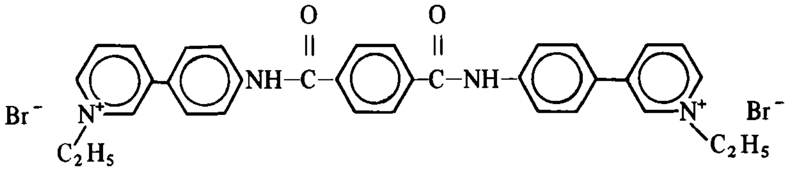
INTRODUCTION

Polymers containing anionic or cationic substituents have been known for a long time and are at present the subject of intensive study [1]. However, the literature contains only a few scattered investigations [2, 3] concerning the properties of polymers with positively charged atoms in the polymeric backbone. These polymers, for which the name ionenes [4] was suggested, are of practical importance since ammonium groups are known to impart pharmacological, bacteriocidal, and other properties. Thus onium salts of the following structure (I) where n is equal to 2 or 10, have been used



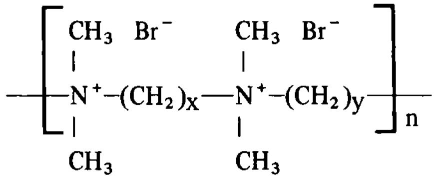
$$(CH_3)_3-\underset{Br^-}{N^+}-(CH_2)_n-\underset{Br^-}{N^+}-(CH_3)_3$$

I



II

extensively as antihypertensive agents [5] while compounds of Structure II have been shown recently to be very powerful antileukemic agents giving life extension of 200-300% at optimal drug levels [6]. It seems that the relatively high molecular weight of II does not impede pharmacological activity and this is also true for ionene polymers (Structure III) of molecular weight 10,000-40,000



$$\left[-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}-(CH_2)_x-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}-(CH_2)_y-\right]_n$$

III

which have been found to inhibit bacterial growth of E. coli and S. aureus in concentrations as low as 5 μg/ml [7].

Polymers represented by Structure III are water soluble and combine with heparin to yield insoluble polyelectrodyte complexes. The latter, however, are not endowed with desirable mechanical characteristics which would permit their utilization as nonthrombogenic structural materials. Fortunately, by decreasing the concentration of quaternary groups in the polymeric backbone and by making use of the urethane reaction, a series of elastomeric materials of high tensile strength may be synthesized.

Heparin may be grafted on the surface of these polymers because of ionic bond formation between positive nitrogens and negative sulfonates according to a mechanism previously reported by a number of investigators [8, 9]. The present paper also describes methods of carrying out such grafts. The heparinized samples were found to be nonthrombogenic by whole blood and plasma tests.

Thus far the elastomers with wide biomedical application have been the silicones, though they can have problems with low strength or fatigue life, especially in the unreinforced state.

If elastomers are to find wide biomedical application, the user must develop a good appreciation of their mechanical response and, more importantly, of how the structure can be tailored to improve the properties where necessary. Hence, one of the purposes of this paper is to show how such properties are characterized and some of the conclusions which can be deduced from such studies.

II. SYNTHESIS

Elastomeric ionenes may be prepared from commercially available materials: (A) polyhydroxy prepolymers reacted with disocyanates first and then with di- or tetramethylamino alcohols to give amino prepolymers,

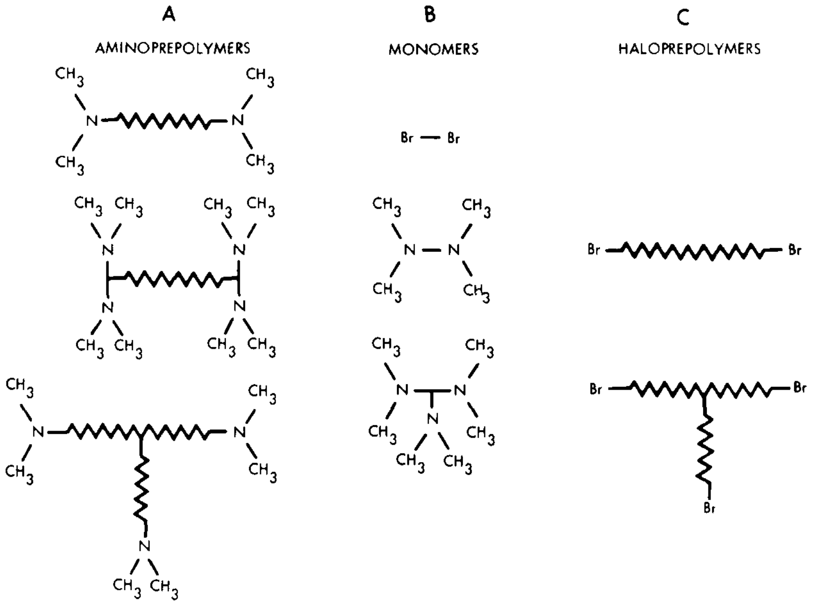
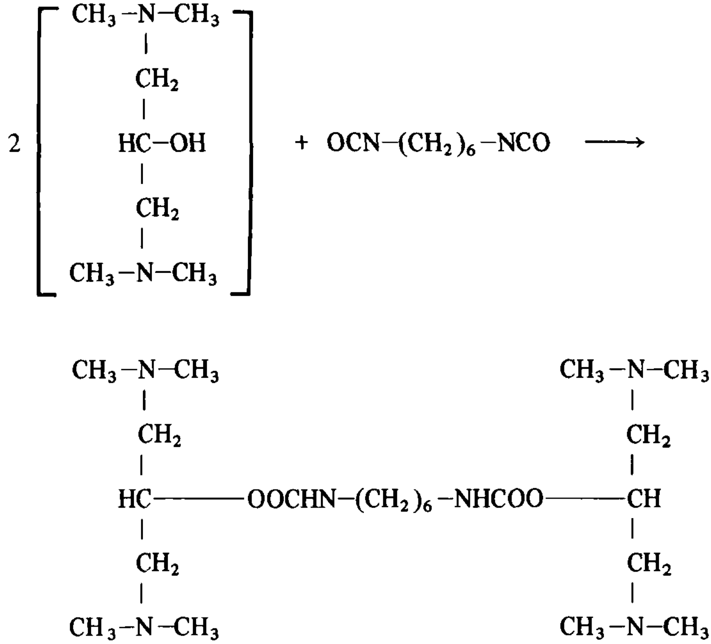


Fig. 1. General scheme for the synthesis of elastomeric ionenes.

(B) tetramethyl or hexamethylamino alkanes, and (C) halo prepolymers such as dibromopolybutadienes or halo prepolymers formed by reacting polyisocyanates with halo alcohols. These three classes of materials are shown schematically in Fig. 1. It is thus possible to obtain a very large number of homo or block polymers of elastomeric nature with a variable concentration of positive charges as well as of hydrophilic and hydrophobic segments by A-B, B-C, and C-A reactions. With a proper choice of reagents, linear or cross-linked clastomers are synthesized. For example, a diisocyanate reacted with a tertiary amino alcohol will form a ditertiary amine. When the alcohol contains more than one tertiary amino group, the corresponding reaction product will contain amino groups in excess of the number necessary to form a linear polymer, and these pendant groups would be available for cross-linking the polymer. This is illustrated by the Reaction (1) of bis 1,3-(dimethylamino)-2 propanol and hexamethylene diisocyanate.

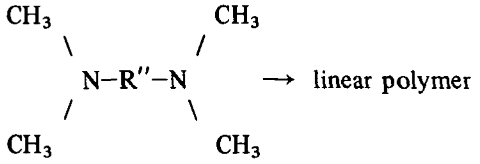


$$2\left[\begin{array}{c} CH_3{-}N{-}CH_3 \\ | \\ CH_2 \\ | \\ HC{-}OH \\ | \\ CH_2 \\ | \\ CH_3{-}N{-}CH_3 \end{array}\right] + OCN{-}(CH_2)_6{-}NCO \longrightarrow \qquad (1)$$

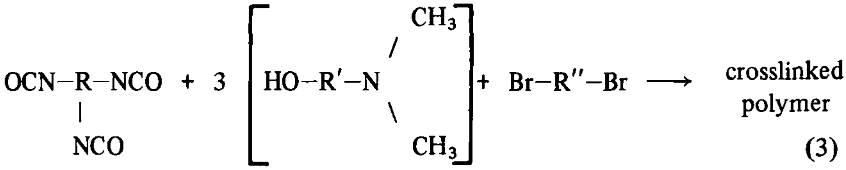
$$\begin{array}{c} CH_3{-}N{-}CH_3 \\ | \\ CH_2 \\ | \\ HC \\ | \\ CH_2 \\ | \\ CH_3{-}N{-}CH_3 \end{array}{-}OOCHN{-}(CH_2)_6{-}NHCOO{-}\begin{array}{c} CH_3{-}N{-}CH_3 \\ | \\ CH_2 \\ | \\ CH \\ | \\ CH_2 \\ | \\ CH_3{-}N{-}CH_3 \end{array}$$

Each hydroxy group adds to an isocyanate group to form a urethane linkage. Further reaction with, e.g., dibromobutane, results in quaternization of the nitrogen atoms and chain extension to form a cross-linked network. Other specific reaction schemes leading to cationic viscoelastic polymers are represented by the general Reactions (2) and (3).

$OCN{-}R{-}NCO + 2(OH{-}R'{-}Br) \longrightarrow Br{-}R'OOCNH{-}R{-}NHCOOR'{-}Br$ +



$$\begin{matrix} CH_3 & & CH_3 \\ \backslash & & / \\ & N{-}R''{-}N & \\ / & & \backslash \\ CH_3 & & CH_3 \end{matrix} \longrightarrow \text{linear polymer} \qquad (2)$$



$$\begin{matrix} OCN{-}R{-}NCO \\ | \\ NCO \end{matrix} + 3\left[\begin{matrix} & CH_3 \\ & / \\ HO{-}R'{-}N & \\ & \backslash \\ & CH_3 \end{matrix}\right] + Br{-}R''{-}Br \longrightarrow \begin{matrix}\text{crosslinked} \\ \text{polymer}\end{matrix} \qquad (3)$$

It is obvious that these reactions may be varied to yield virtually an unlimited number of positively charged materials of different properties. Since some of these possess good mechanical strength and may be cast into thin films, they represent a new class of cationic membranes, and since the cationic groups bond with heparin, the elastomeric ionenes show promise as nonthrombogenic materials for artificial organs.

The preparation of a selected ionene elastomer is based on the reaction of a glycerol ester of ricinoleic acid (Solithane 113, Fig. 2, Structure IV) with a tetramethylamino alcohol and subsequently with dibromopolybutadiene. The reaction product is a cross-linked elastomeric block polymer exhibiting strong birefringence and will be referred to as ionene SPSA3.

Another block polymer was synthesized by reacting IV with n-bromopropanol and then with tetramethylamino polypropylene glycol. The product of this reaction is also a cross-linked elastomeric material and will be referred to as ionene PPGS3.

The third ionene elastomer (DPS4) was prepared by reacting IV with tetramethylamino alcohol and dibromopropane. Figure 2 shows the reactions involved in the preparation of the above three products. The experimental details of the syntheses are as follows.

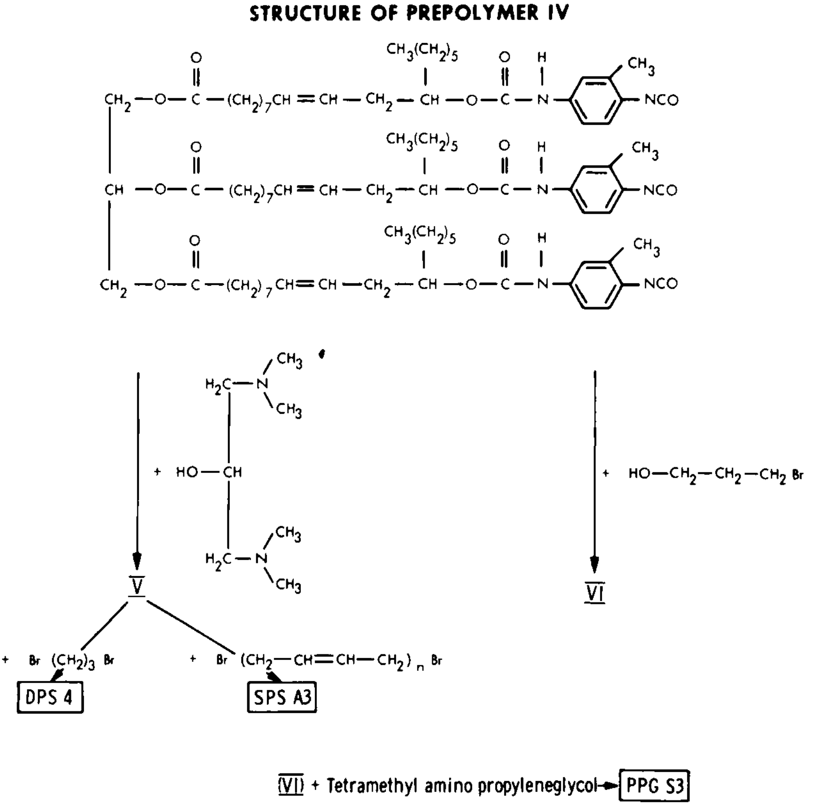


Fig. 2. Synthesis of samples DPS4, SPSA3, and PPGS3.

A. Ionene SPSA3

Solithane 113 from Thiokol Corporation (290.4 g) was dissolved in dry benzene (1100 g). Dry 1,3-bis(dimethylamino)-2-propanol (85.2 g) was added to this solution and the mixture was heated at 50° for 24 hr. The disappearance of the absorption peak at 4.57 μ was utilized to indicate reaction completion. A portion of the reaction product (17.1 g) was reacted at room temperature with dibromopolybutadiene (from Polymer Corporation, Canada) of approximate molecular weight 3500 (35 g) dissolved in benzene (86 g).

B. Ionene PPGS3

Solithane 113 (197.2 g) was mixed with 3-bromo-1-propanol (62.8 g)

Table 1. Properties of Elastomeric Ionenes

Sample	% ionic bromine[a]	Tensile strength[b] (psi)	Elongation at break[b] (%)	T_g[c] (°C)
SPSA3	2.6	255	380	-80
PPGS3	4.3	954	270	-20
DPS4	12.9	2180	85	+40

[a] Potentiometric titration of AgBr.
[b] Ambient temperature, 0.9^{-1} nominal strain rate, dumbbell specimens.
[c] Estimated from Fig. 5.

and heated first at 60°C for 48 hr and then at 80° for 8 hr. The reaction was followed by means of ir (4.57 μ). Dry polypropylene glycol 2000 (127.5 g) from Union Carbide was mixed with freshly distilled 2,4-tolylene diisocyanate (22.2 g) and kept at 60°C for 24 hr. The reaction was followed by means of the 2.85 μ absorption peak in the ir spectrum. On completion of the reaction bisdimethylamino-2-propanol (18.64 g) was added and reacted at 60°C for 3 hr. The disappearance of the 4.7 μ peak indicated the end of reaction. The reaction products of Solithane and polypropylene glycol (34.6 and 39.6 g, respectively) were then intimately mixed with benzene (170 cc), filtered through glass wool, and poured into a Teflon mold. After evaporation of the solvent the sample was cured at 60°C for 14 hr. The final product was obtained in the form of a rubbery sheet 2 mm thick.

C. Ionene DPS4

Solithane 113, reacted with bisdimethylamino-2-propanol (185.2 g), was mixed with dry benzene (1100 g) and heated at 60°C for 4 hr. A portion of this solution (51.2 g) was mixed with 1,3-dibromopropane (6.06 g), filtered through glass wool, and poured into a Teflon mold. After evaporation of the solvent a leathery 2-mm thick sheet was obtained.

Some properties of the above three specimens are shown in Table 1.

III. HEPARINIZATION

Ionene SPSA3 was immersed in a 2% solution of heparin (from Abbott Laboratories) in water/methanol (1:1 by volume) or water/tetrahydrofuran

(1.1 by volume) for 12 hr. After repeated washings with distilled water, the samples were found to be nonthrombogenic, i.e., no clots were observed for 1 hr when whole human blood (0.5 cc) was placed on the surface (1 cm^2) of the specimen. This was not due to extraction of heparin by the blood because when the latter was removed from ionene SPSA3 it clotted in contact with glass in the normal way.

Electron scanning microscope (esm) was used to show the presence of heparin on the surfaces. This was accomplished by cutting the specimens into two parts, heparinizing one part and using the other part as control. After matching the cut areas, esm photographs were obtained (Figs. 3 and 4).

IV. VISCOELASTIC PROPERTIES

In examining the viscoelastic properties, three principal experimental techniques were employed: the Gehman shear modulus-temperature studies, differential scanning colorimetry, and stress relaxation.

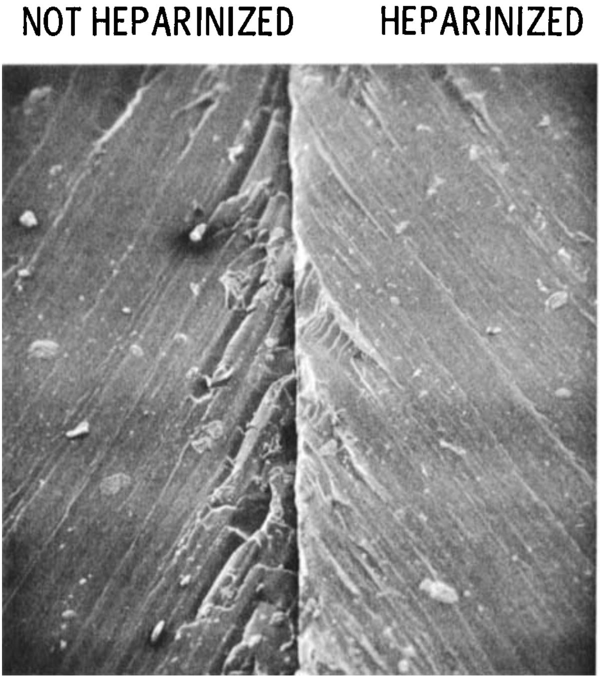


Fig. 3. Electron scanning microscope pictures of SPSA3 ionene. 100X.

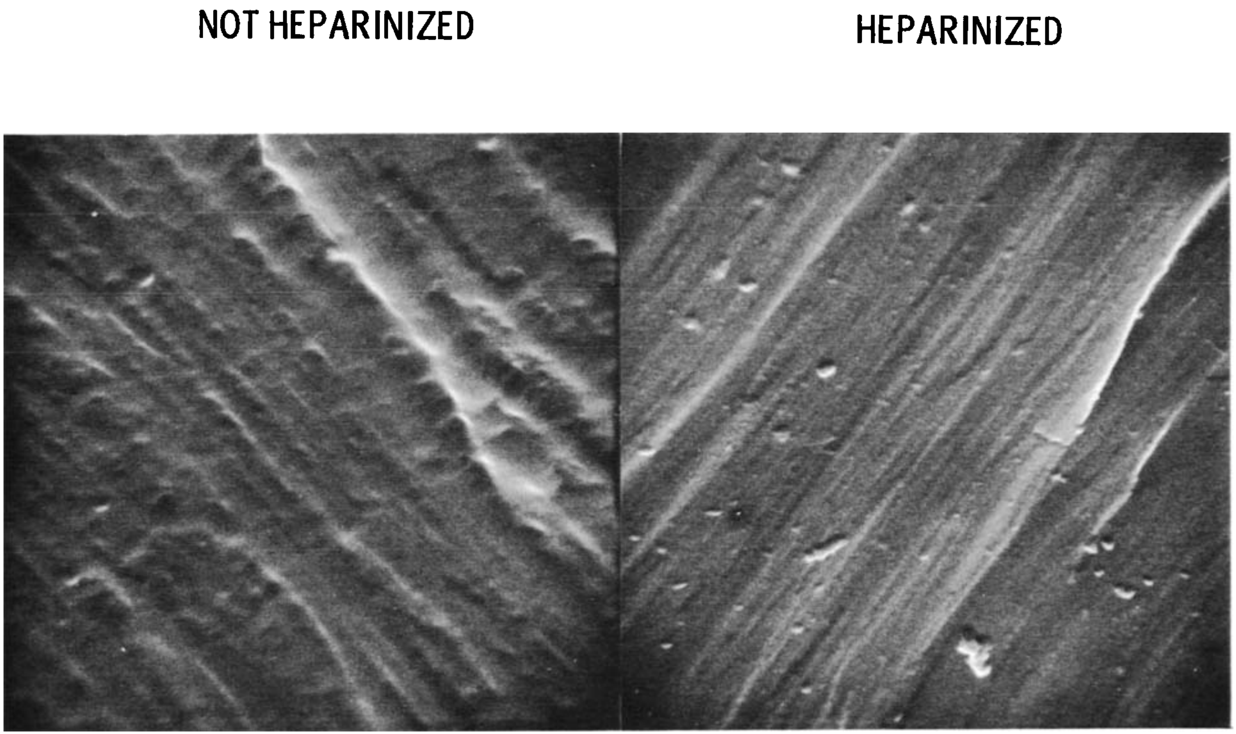


Fig. 4. Electron scanning microscope picture of SPSA3 ionene. 5000X.

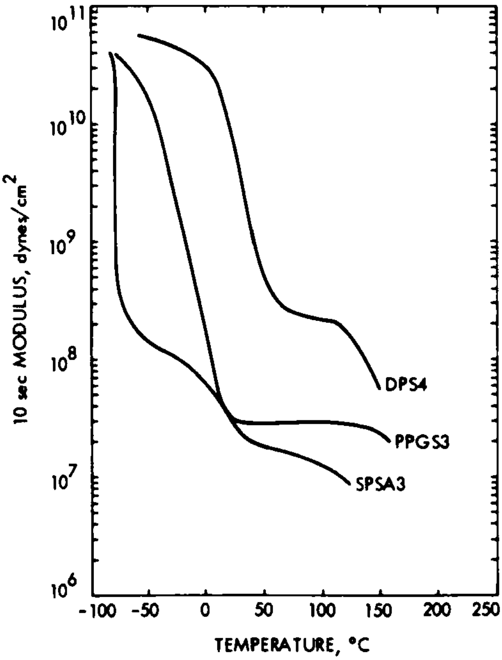


Fig. 5. Modulus versus temperature of samples DPS4, SPSA3, and PPGS3.

A. Shear Modulus-Temperature Curves

Ten second shear moduli were determined as a function of temperature by means of a Gehman apparatus [10]. The technique is used to make comparisons of the effect of changes in the backbone structure on the properties. Figure 5 shows the effect of changing the length of the hydrocarbon chain in the dibromide in the comparison between SPSA3 (dibromopolybutadiene) and DPS4 (dibromopropane). The T_g is raised ca. 120°. This is due to both the shortening of the chains between cross-links and the increased intermolecular forces from the higher concentration of ammonium groups. (Of course, there will also be a contribution to this change associated with the fact that one has a saturated component and the other an unsaturated component). Also shown is the effect of changing the dibromide backbone from a hydrocarbon to a polyether, PPGS3 (dibromopolypropylene glycol) with little change of the cation content. Here T_g is raised by only 60°C above that of SPSA3. Finally, the effect on the modulus and

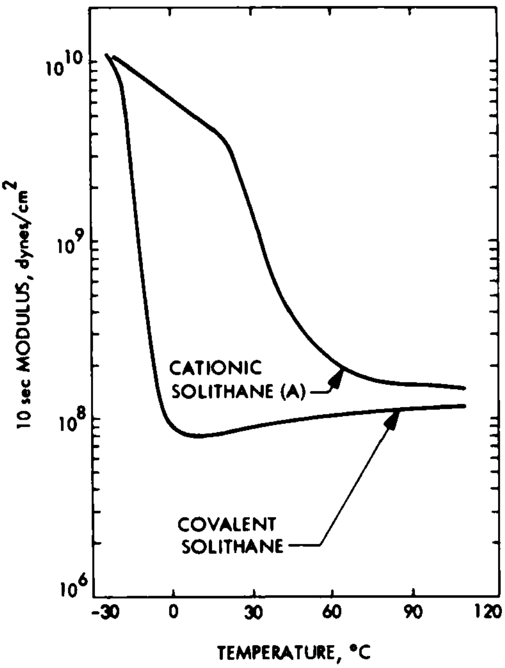


Fig. 6. Modulus versus temperature of a covalent and cationic solithane (DPS4).

T_g of introducing the charged groups is indicated by the location and shape of the Solithane curve in Fig. 6. Here the modulus of Solithane cured with castor oil, hence devoid of positive charges, is compared with the modulus of the same material containing ammonium groups. The presence of the positive charges apparently serve to raise the T_g as well as the rubbery modulus.

B. Differential Scanning Calorimetry

Data were taken by a Perkin-Elmer DSC-1 Differential Scanning Calorimeter. The temperature range covered in this study was -100 to + 100°C at a heating rate of 10°C/min. Throughout the experiment the sample was under the constant purge of a stream of dry nitrogen.

Figure 7 shows the DSC thermogram for ionene SPSA3. The rise initiated near -80°C can be safely attributed to the glass transition of the polybutadiene blocks. The second rise near 10°C, which is broader and lower in strength, could be attributed to the Solithane blocks. The final rise near 80°C is not associated with any transitions, but is probably the onset of the chemical scission of the weak urethane linkages. This rise does not taper off at higher temperatures but continues up to at least 150°C (not shown in Fig. 7). It was shown by Colodny and Tobolsky [11] that the chemical effects may be attributable to the reaction of the disubstituted urea and biuret linkages.

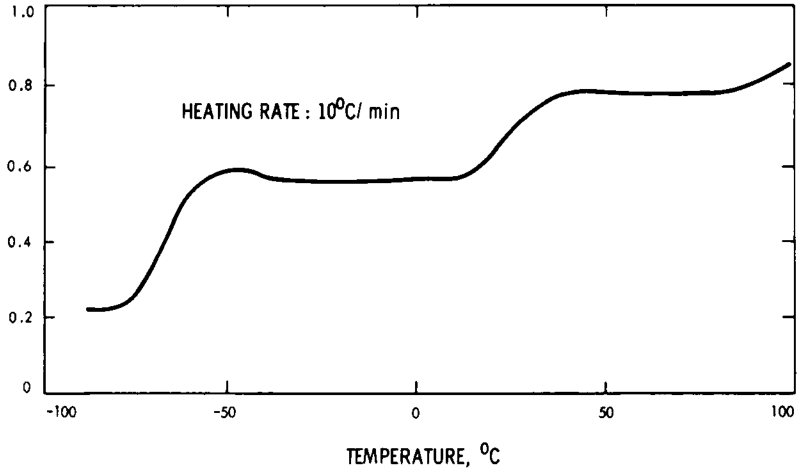


Fig. 7. Differential scanning calorimetric thermogram for SPSA3 ionene. Heating rate 10°C/min.

C. Stress Relaxation

The automatic stress relaxometer employed in this work has been described previously [12]. A Checktronics Environmental Test Chamber was used to provide the temperature range of -150 to +150°C for the modulus-time measurements. Constancy of the temperature was approximately ±1/4°C. In the temperature range where the sample exhibits values of the modulus less than 5 X 10^8 dynes/cm^2, uniaxial tensile measurements were made. At lower temperatures where the sample becomes increasingly glassy

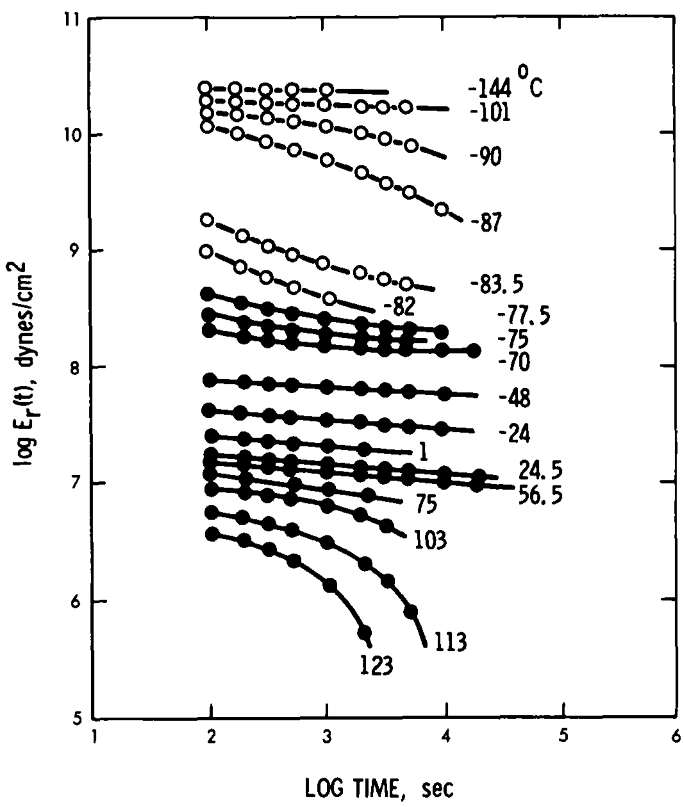


Fig. 8. Isothermal modulus-time curves for SPSA3 ionene.

and the modulus exceeds the above value, a flexural mode was found to be more accurate [13]. The sample was supported at the ends by knife edges on the lower clamp of the relaxometer, and the strain was applied by another knife edge at the center of the sample. The latter knife edge was connected through the upper clamp to the load cell. Isothermal modulus-time curves were obtained by procedures that have been well-documented in the literature [14, 15].

Isothermal modulus-time curves at 18 temperatures are reproduced in Fig. 8. Here the open circles were those taken by flexural experiments and the closed circles by tensile experiments. Good agreement can be seen between these two techniques. Two types of information may be deduced from these data; namely, the effects of temperature and time on relaxation

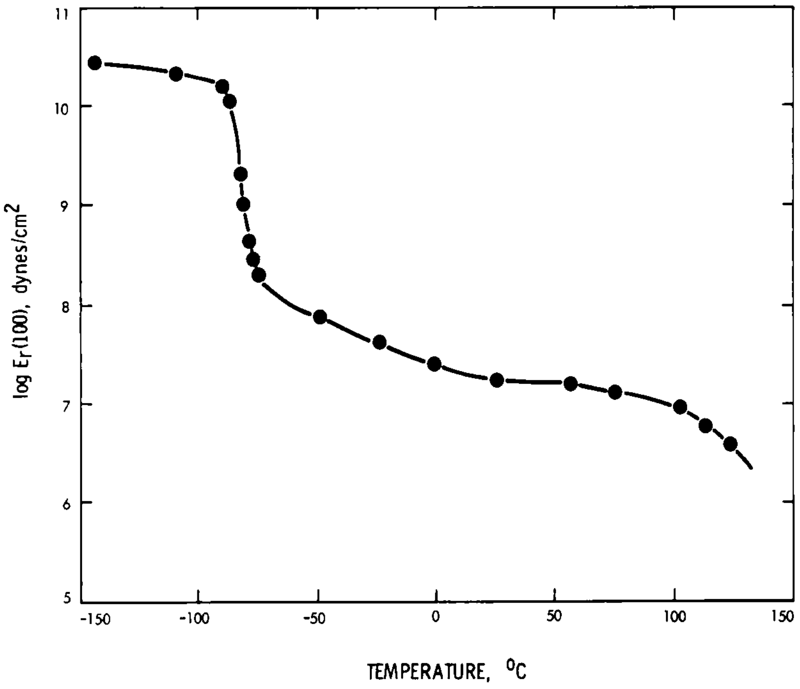


Fig. 9. Isochronal modulus-temperature curve for SPSA3 ionene. Reference time scale: 100 sec.

moduli. First, by taking 100 sec. as a reference time scale, cross-plotting yields the modulus-temperature curve for this material (Fig. 9). At the low temperature end the modulus is above 10^{10} dynes/cm^2, which is characteristic of glassy polymers. Above -100°C a drop in $E_r(100)$ occurs. The temperature at which the modulus becomes 10^9 dynes/cm^2 may be defined as the inflection temperature [13] (T_i). It was demonstrated by Tobolsky [14] that T_i is closely related to T_g. For this ionene, $T_i = -82°C$, which is close to the T_g observed in the DSC thermogram and in the Gehman test (Fig. 5).

In ordinary homopolymers the value of $E_r(100)$ above T_i should be in the region of 10^6-10^7 dynes/cm^2. For our sample the modulus immediately above T_i is of the order of 10^8 dynes/cm^2, which is an order of magnitude greater. This is indicative of the block copolymer structure of the SPSA3 ionene. Above -80°C only the polybutadiene blocks are in the rubbery state, while the Solithane blocks remain glassy, thus contributing to higher

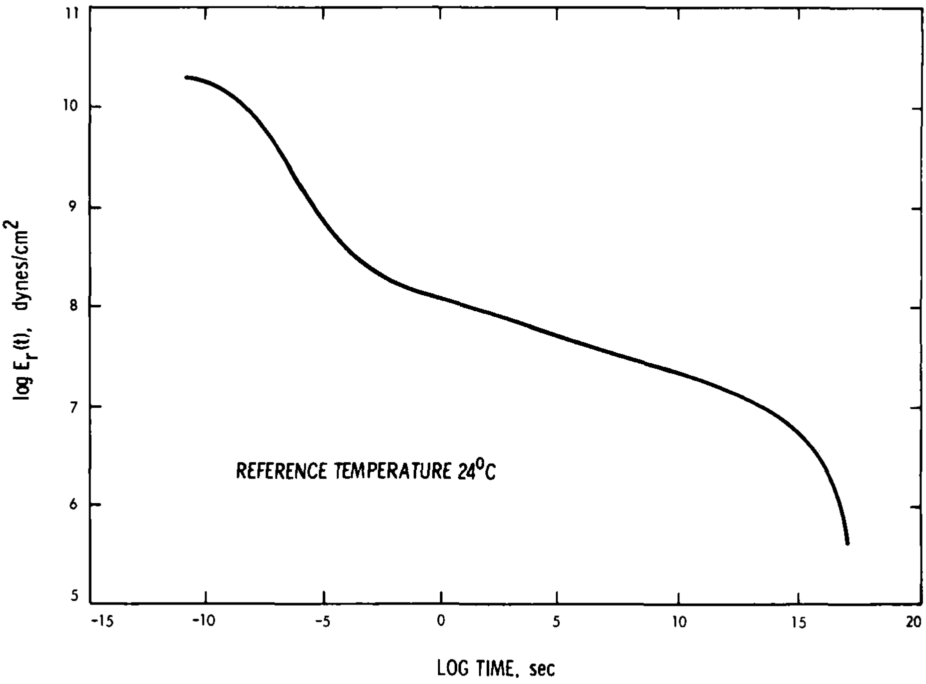


Fig. 10. Master curve for SPSA3 ionene. Reference temperature: 24°C.

modulus. As the temperature is raised there is a continuous decrease in $E_r(100)$ until about 20°C, where it levels off around 10^7 dynes/cm^2. This temperature region is just where the DSC thermogram exhibits the second transition. Above 20°C the entire sample presumably is in the rubbery state, i.e., both polybutadiene and Solithane blocks are rubbery.

As temperature continues to increase to near 100°C, another drop in modulus begins. Here the drop is due to the chemical stress-relaxation effects of the urethane linkages. Again we note in Fig. 7 that above 80°C there is a continuous rise in the thermogram, attributed to chemical reactions.

The time effect on the relaxation modulus can best be studied by the construction of the master curve via the Time-Temperature Superposition Principle [14, 16]. Figure 10 shows the master curve for ionene SPSA3 covering 30 decades of time (reference temperature 24°C). Again we see that at short times the sample exhibits the typical glassy and transition zone behavior. At intermediate times the modulus decreases by about an

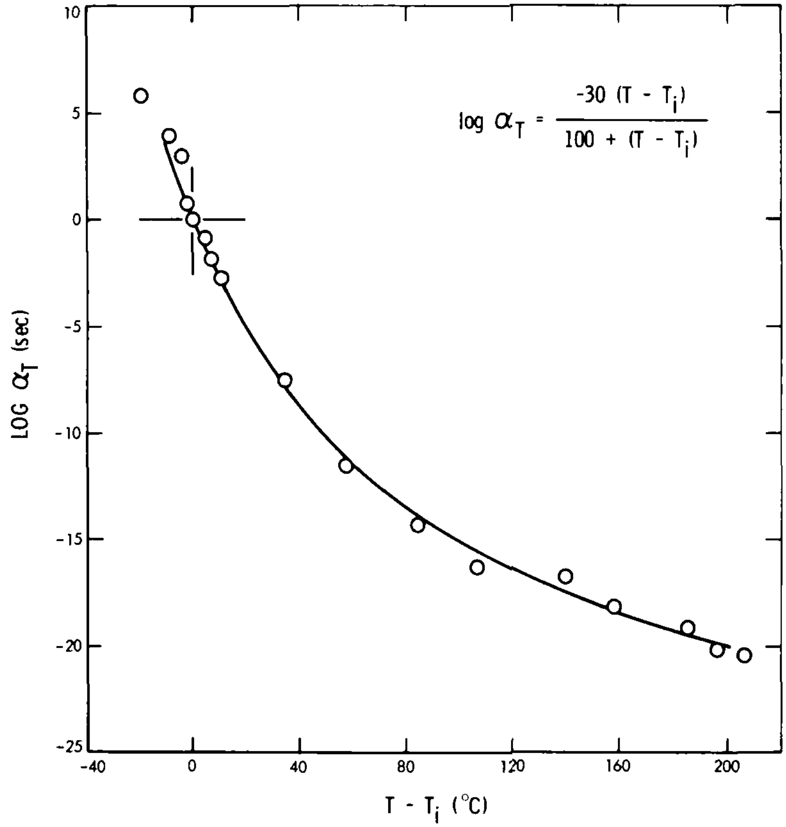


Fig. 11. Semilogarithmic plot of the shift factor (a_T) against T − T_i. Solid curve was calculated by the WLF equation (Eq. 1) with c_1 = 30 and c_2 = 100.

order of magnitude (from 10^8 to 10^7 dynes/cm^2) in nearly 20 decades of time. Flow commences at the long time end. Since our sample is crosslinked, the mechanism is due to chemical scission of chains rather than chain slippage.

We note that the second transition near 20°C observed in both the DSC thermogram and the modulus-temperature curve is not evident in the master curve. It is possible that this transition, being very broad, is not distinguishable from the gradual decrease in $E_r(t)$ in the intermediate time region. To further scrutinize this transition, we plot the shift factors, a_T, against the T − T_i in a semilogarithmic plot (Fig. 11). We note that there is a discontinuity between 90 and 140°C above T_i, which is just the room temperature region. In the absence of further data, we can only say that the reason we do not observe the second transition may be due to the difficulty encountered in constructing the master curve by time-temperature superposition.

The data in Fig. 11 can be fitted to the well-known WLF equation [16]:

$$\log a_T = \frac{-c_1(T - T_i)}{c_2 + (T - T_i)} \tag{4}$$

In Eq. (4) we have taken T_i as the reference temperature. On the basis of free volume theory, the parameters c_1 and c_2 have the following meaning [12]

$$\begin{aligned} c_1 &= 1/2.303f_g \\ c_2 &= f_g/\beta_f \end{aligned} \tag{5a}$$

where f_g is the fractional free volume at the glass transition and β_f is the thermal expansion coefficient of the free volume. Strictly speaking, the above parameters are meaningful only if the glass transition temperature was used as the reference temperature. However, due to the proximity of T_i to T_g, and the agreement between the transition temperatures determined by DSC and modulus-temperature plot, we feel that T_i is an adequate substitute. To provide the best fit between Eq. (4) and the data in Fig. 5, we find that $c_1 = 30$ and $c_2 = 100$. These numbers are considerably greater than the "universal values" of 17.4 and 51.6 for most homopolymers [16]. In terms of the packing, we find that our block copolymer possesses a fractional free volume of 0.015 rather than 0.025 for homopolymers, and the thermal expansion coefficient for the free volume is in this instance 1.5×10^{-4} in comparison with the "universal" value of 4.8×10^{-4}.

The smaller values of f_g and β_f are consistent with the block copolymer nature of our ionene sample. At -80°C only the polybutadiene blocks pass into the rubbery state whereas the Solithane blocks remain in the glassy state. Thus one would expect a smaller fractional free volume at the first transition. Similarly, since β_f is just the difference between thermal expansion coefficients of the sample in the rubbery and glassy states, its value can be expected to be smaller as long as part of the sample remains in the glassy state. It is important to note that values of c_1 and c_2 for styrene-butadiene-styrene (SBS) block copolymers are closer to the universal values [17-19]. However, the shape of the WLF plot shows a more pronounced break at the second T_g for the SBS block copolymer than for the SPSA3 ionene. It appears that since there is phase separation in the former, the styrene domains do not participate in the relaxation processes at temperatures below their T_g. There is perhaps no clear-cut phase separation for the ionene. As a consequence the Solithane segments may have contributed to the relaxation processes below their T_g. The total a_T factor is thus due to contribution from both components and hence is larger than expected.

A second possible explanation is that the enhanced intermolecular forces due to the cationic groups and their counter ions are modifying the response. This is certainly true, as evidenced by the results of Fig. 6, yet it is doubtful that such forces can offset c_1 and c_2 because Tobolsky and Shen [20] found that the introduction of hydrogen bonds did not modify the "universal" values in polymethacrylates.

V. ULTIMATE PROPERTIES

Ring-shaped specimens (3/4 in. i.d. X 1.0 in. o.d.) were cut from the same sheet of SPSA3 used in the stress relaxation or DSC measurements. Tensile tests were carried out in the conventional manner at two rates at each of seven temperatures from +110 to -60°C. The stress-strain curves were not extrapolated to obtain the break properties at the inner diameter. The results are shown as a failure envelope in Fig. 12. This is a plot of the breaking stress, normalized for temperature effects to 20°C, against the breaking strain (in logarithmic coordinates). For conventional amorphous elastomers, break data plotted in this way give a single smooth curve concave to the stress axis [21]. The stress-at-break, σ_b, increases steadily with decreasing temperature while the strain-at-break, ϵ_b, passes through a maximum. In the present case the tests could not be performed to low enough temperatures to cause ϵ_b to pass through this maximum and so only a portion of an envelope has been obtained.

The present data are more scattered than is usually the case. Additional data are being obtained, but on another preparation. Since it is not yet clear how reproducible the properties will be, it seems preferable to consider only data obtained from a single sheet of rubber.

Over the limited range of strain rates and temperature studied, the ultimate properties do not show any marked effect of the second or room temperature transitions seen in DSC and in the Gehman tests, though the slow strain

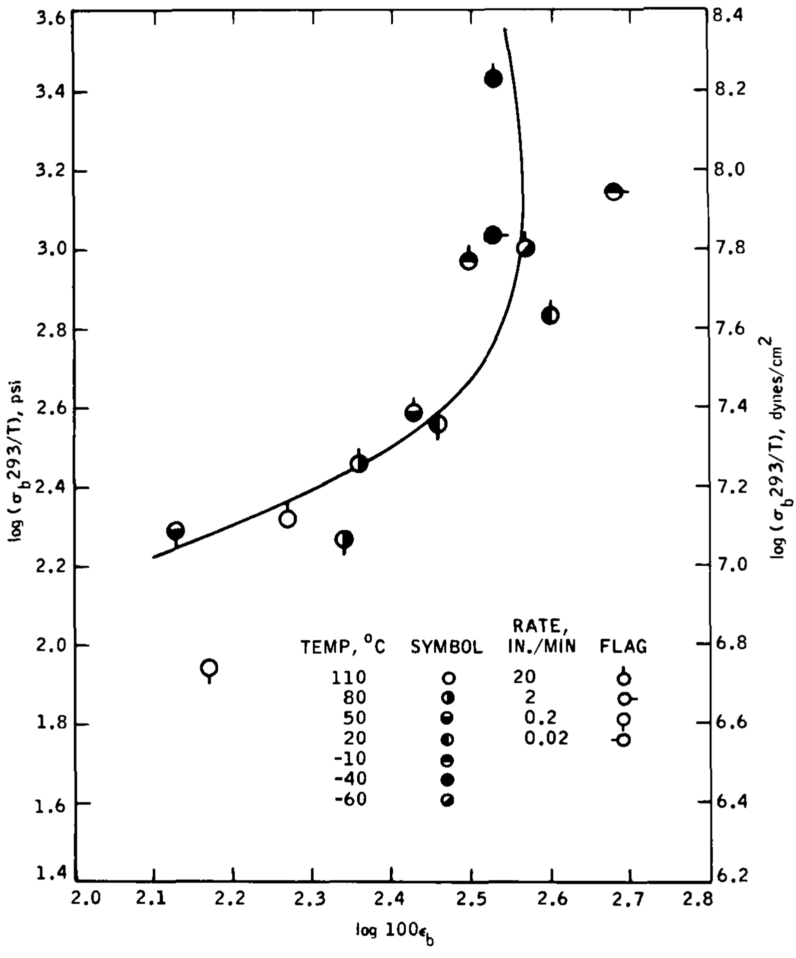


Fig. 12. Failure envelope for SPSA3 ionene.

rate data at the two highest temperatures do appear to be shifted toward higher values of σ_b. To show more clearly that the Solithane transition does not affect ultimate properties, we may examine their time dependence. These can be obtained under the assumption that the a_T value determined from the stress relaxation data will also apply to the ultimate properties, as found by Smith [22] for simple elastomers. Thus plots of log $\sigma_b T_0/T$ or log ϵ_b vs log t_b/a_T should superpose to give reasonably smooth curves.

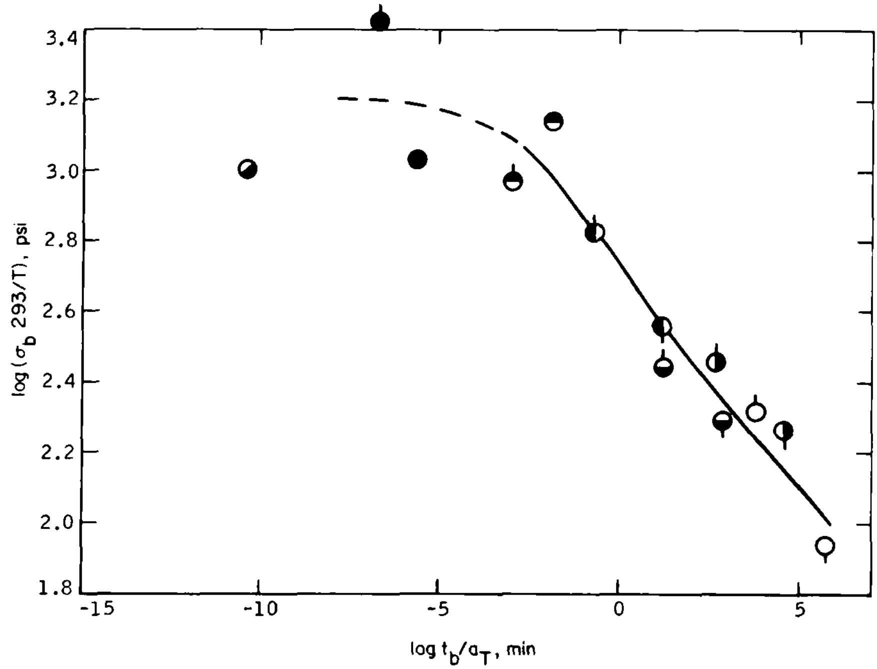


Fig. 13. Ultimate stress vs breaking time for SPSA3 ionene.

Here t_b is the time to break. Figures 13 and 14 show the results of such plots, and the results do indeed give reasonably smooth curves and the response is as though only one transition were acting. Thus the ultimate properties do not seem to have been markedly modified by the softening of the glassy Solithane blocks as the temperature is increased. Perhaps the domains which they form are too small to be rigid at low temperatures, so that they deform under stress and hence cannot modify the response, as discussed previously.

It is possible to deduce an average cross-link concentration, expressed as the number of effective chains/cm^3, ν_e, by comparing the shape of the failure envelope plot with a theoretical envelope based on the inverse Langevin function [23, 24]. The value thus estimated is 220×10^{-6} moles/cm^3. Although this is not a highly reliable value, since the break data are not extensive enough to permit a more accurate estimation, it is essentially correct. Thus, it should also be possible to estimate ν_e from the modulus data in Fig. 5. The value of the modulus at 80°C is about

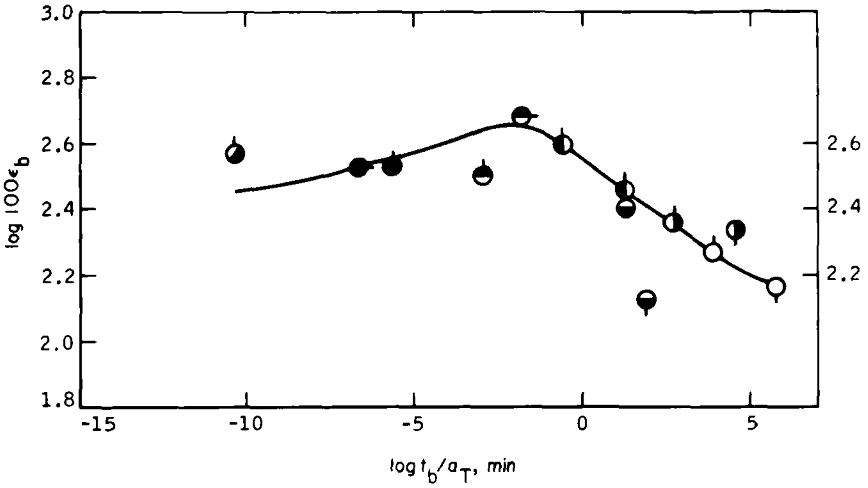


Fig. 14. Ultimate strain vs breaking time for SPSA3 ionene.

1.26×10^7 dyne/cm^2, which on setting $\nu_e = E/3RT$ leads to a value of ν_e of 144×10^{-6} moles/cm^3. For the two values to be in agreement, the curve of Fig. 12 in the region of log $100\epsilon_b = 2.1$ would have to be decreased by 0.2 log units which is entirely reasonable given the paucity of data.

On the other hand, if this discrepancy is substantiated by more complete measurements now in progress, we would tentatively ascribe it to the block copolymer nature of the polymer and to the presence of the quaternary nitrogen atoms. These features of the structure could produce a higher modulus than would be expected on the basis of the actual degree of cross-linking. In other words, these features may play the role of secondary cross-link sites, active at small strains but disrupted as the break point is approached. This is the type of response seen with carboxyl-containing rubbers cured with both zinc oxide and peroxide [25]. Here the zinc carboxylate bonds are labile and break down as the specimens are stretched.

VI. CONCLUSIONS

A new family of linear or cross-linked homo or block polymers containing quaternary nitrogen atoms and therefore capable of bonding with heparin can be synthesized by a very simple procedure. The products may be highly hydrophilic or hydrophobic, of different degree of tensile strength, elongation at break, or glass transition temperature according to the molecular weight and structure of the prepolymers used in the synthesis. Only a few selected samples were investigated, and the mechanical and nonthrombogenic properties of one selected specimen were examined in greater detail. The results appear to be very promising, and it is therefore concluded that the above-described synthesis offers a large reservoir of materials whose properties may be tailored according to requirements.

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