Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kennedy, Joseph P.(1984) 'Synthesis of Telechelic Polymers by Cationic Techniques and Application of the Products', Journal of Macromolecular Science, Part A, 21: 8, 929 — 941

To link to this Article: DOI: 10.1080/00222338408056583

URL: http://dx.doi.org/10.1080/00222338408056583

J. MACROMOL. SCI.—CHEM., A21(8&9), pp. 929-941 (1984)

Synthesis of Telechelic Polymers by Cationic Techniques and Application of the Products

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ABSTRACT

Various linear and three-arm star end-reactive prepolymers carrying one, two or three terminal functions have been prepared by carbocationic techniques. The higher molecular weight varieties of these materials are valuable intermediates for the synthesis of block copolymers, whereas the low molecular weight telechelics (liquid oligomers) are useful starting materials for extension by end-linking. This presentation outlines the synthesis of some new polyisobutylene-based linear and three-arm star, symmetric and asymmetric end-reactive prepolymers such as, α-phenyl-ω-tert chloro-PIB, α,ω-diaryl-PIB's, and their derivatives carrying the $-C_6H_4NO_2$, $-C_6H_4NH_2$, etc. end groups. Telechelic PIB's with $-C_6H_4NH_2$ end groups react with diepoxy compounds (EPON 826) to give rise to hydrolytically and thermally stable flexible networks. An efficient semicontinuous synthesis procedure is outlined that leads to well-defined linear and three-arm star tert.-chloro-telechelic PIB's with close to theoretical end group functionalities and molecular weight distributions. Three-arm star hydroxyl-telechelic PIB's in conjunction with $OCN-C_6H_4-CH_2-C_6H_4-NCO$ give new model polyurethane networks exhibiting outstanding hydrolytic and thermal properties.

INTRODUCTION

End-reactive liquid oligomers (or telechelic prepolymers) can be end-linked to high molecular weight solid products and could be used in highly efficient polymer manufacturing processes, i.e., processes utilizing low shear and/or high speed equipment. Re-

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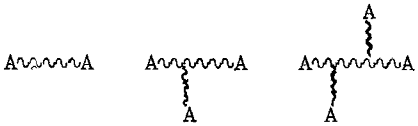
search and development effort in this field is actively pursued all over the world, particularly in Japan and the U.S. This presentation concerns recent advances in the synthesis of end-reactive oligomers by cationic techniques, the characterization of these materials, and some physical-mechanical properties of networks prepared by the use of some new end-reactive prepolymers.

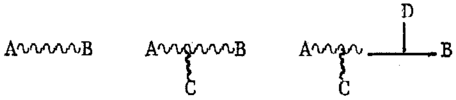
TERMINOLOGY

The term telechelic (from the Greek tele = far, distant and chelos = claw) has been proposed by Uraneck, Hsieh, and Buck (1) some twenty years ago to describe polymers carrying two functional end groups. The field of telechelic polymers and oligomers has recently been reviewed (2,3).

I wish to broaden the scope of the term telechelic to include not only terminally functional linear polymers (as implied by Uraneck et al.) but also branched polymers (4). Further, I propose to distinguish between homotelechelic (or simply telechelic) polymers, the terminal functions (A) of which are identical:

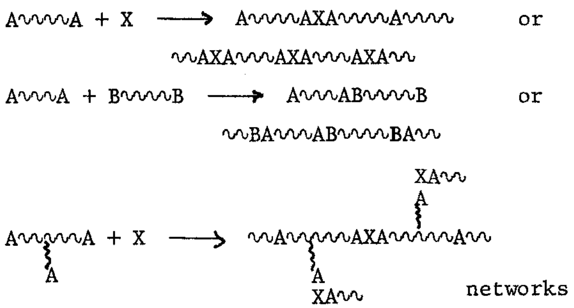


and heterotelechelic or asymmetric telechelic polymers, the terminal functions (A,B,C...) of which are dissimilar:



This terminology only concerns end groups and does not indicate the nature of the polymer that carries the end groups. The polymer may be linear or branched, it may be a homopolymer, random copolymer, block or graft copolymer, or any complex assemblage of segments. The symbol $\overline{F}_n$ will express the number average end groups. A linear polymer may have $\overline{F}_n$ = 1.0 (if only one terminus is functional) or $\overline{F}_n$ = 2.0; if it is branched $\overline{F}_n$ = 2,3,4,...

The terminal group may be any kind of reactive function, such as -OH, $-NH_2$, -NCO, $-CH=CH_2$, -SH, -CHO, $-CH\overset{O}{\frown}CH_2$, -COOH, $-\overset{|}{\underset{|}{Si}}H$, etc., suitable for further derivatization or end-linking either directly or by means of linking agent (X), and thus may give rise to linear or crosslinked high molecular weight structures:



Polymers that carry relatively unreactive end groups, e.g., methyl, cyclohexyl, are not regarded as telechelic species.

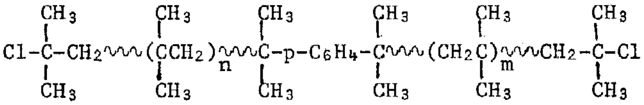
The adjective telechelic is used after the function it refers to, e.g., alcohol-telechelic, amine-telechelic, and it defines a molecule that carries alcohol or amine end groups.

Telechelic can also be used as a noun in which case it describes a polymer that carries at least two functional end groups or at the most as many functional end groups as it has extremities.

By convention, intermediates that arise during step growth polymerizations (i.e., intermediates that form during polycondensations that lead to nylons, polyesters, etc.,) fall outside the scope of telechelic systems. Typical telechelics are, for example, liquid diols used for the synthesis of polyurethanes or certain diepoxides used for the epoxy resin manufacture.

TELECHELIC POLYISOBUTYLENES

Increased insight into the detailed mechanism of olefin polymerizations in general and isobutylene polymerization in particular led to the proposition that the end groups of polyisobutylene PIB could be exactly controlled by the use of special initiator-chain transfer agents, so called inifers (5). Extensive evidence has been presented that demonstrates linear PIB's carrying exactly two $-CH_2C(CH_3)_2Cl$ end groups can be obtained by polymerizing isobutylene in the presence of BCl_3 coinitiator and $ClC(CH_3)_2$-pC_6H_4-$C(CH_3)_2Cl$ (p-dicumyl chloride, pDCC) inifer in various solvent systems at moderately low temperatures (6):



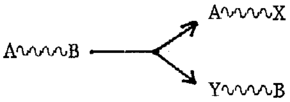
$$\text{Cl-}\underset{CH_3}{\overset{CH_3}{C}}\text{-CH}_2\sim\sim(\underset{CH_3}{\overset{CH_3}{C}}CH_2)_n\sim\sim\underset{CH_3}{\overset{CH_3}{C}}\text{-p-}C_6H_4\text{-}\underset{CH_3}{\overset{CH_3}{C}}\sim\sim(CH_2\underset{CH_3}{\overset{CH_3}{C}})_m\sim\sim CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-Cl}$$

chlorine-telechelic PIB $({}^{\overline{t}}\text{Cl-PIB-Cl}^{\overline{t}})$

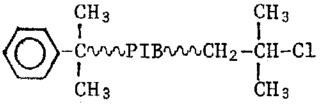
This and three-arm star telechelic PIB's are most intriguing new materials that could find applications in a large number of areas. Low molecular weight ($\overline{M}_n$ = 1000-10,000) PIB's are liquids whereas the higher molecular weight products are solid rubbers exhibiting an excellent combination of physical-mechanical-chemical properties at a modest cost.

ASYMMETRIC TELECHELICS AND THEIR DERIVATIVES

The great advantage of asymmetric telechelics over symmetrical species is that the end groups A and B of the formers can be derivatized independent of each other:



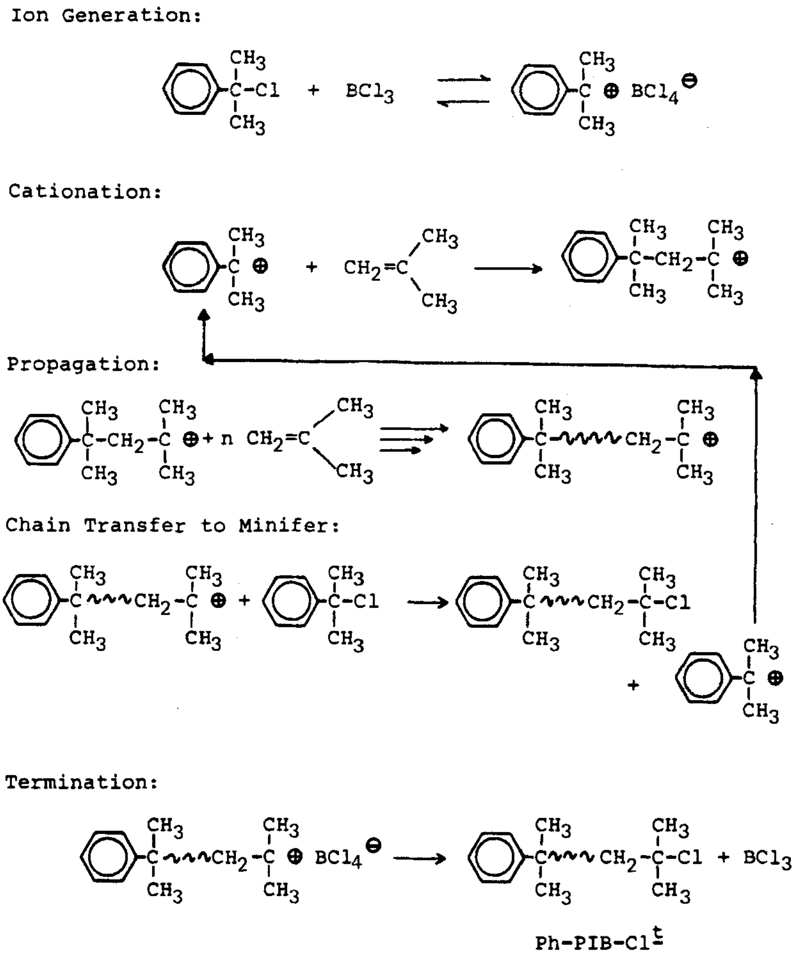
Recently a new family of well-defined asymmetric telechelic materials has been developed starting with α-phenyl-ω-t-chloropolyisobutylene (7):



$$C_6H_5\text{-}\underset{CH_3}{\overset{CH_3}{C}}\sim\sim PIB\sim\sim CH_2\text{-}\underset{CH_3}{\overset{CH_3}{CH}}\text{-Cl}$$

Ph-PIB-$\text{Cl}^{\overline{t}}$

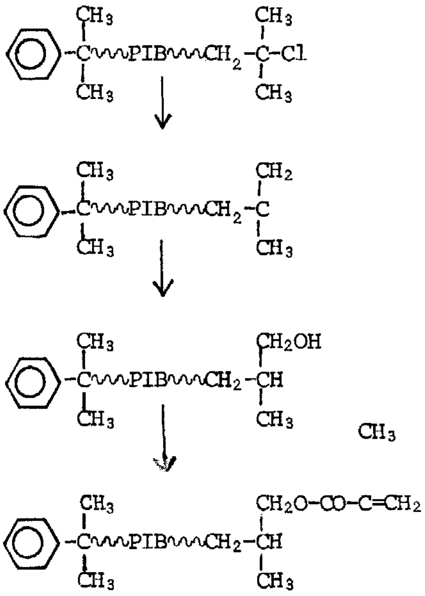
This key intermediate was synthesized with the cumyl chloride/BCl_3/isobutylene minifer system (monofunctional initiator-transfer agent). The mechanism of the polymerization is outlined in Scheme I (8):



Scheme I

Synthesis of α-Phenyl-ω-tert.-Chloropolyisobutylene by the Minifer Technique

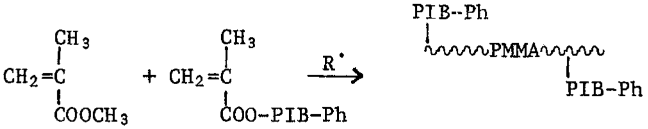
Both end groups, the α-phenyl and the α-t-chloro functions, can be used for a variety of derivatizations. For example, the t-chloro terminus can be subjected to quantitative dehydrochlorination with t-BuOK in refluxing THF, the exo olefin thus obtained can be quantitatively hydroborated/oxidized to the corresponding primary alcohol, which in turn can be quantitatively converted with methacroyl chloride in the presence of triethylamine in THF to a new macromer, α-phenyl-ω-methacryloyloxy-polyisobutylene (8):



Ph-PIB-MA

The latter macromer can be homopolymerized and/or copolymerized with conventional acrylates by conventional free radical initiators to interesting new graft copolymers (8). The homopolymerization of a relatively low molecular weight Ph-PIB-Ma macromer ($\overline{M}_n$ = 5200) (AIBN, 60°C, bulk, 72 hrs) gave a very high molecular weight product ($\overline{M}_v \sim 6.8 \times 10^5$ daltons) (8).

The copolymerization of Ph-PIB-MA with methyl methacrylate has been investigated (AIBN, benzene, 60°C, 10 hrs). Copolymerization occurred readily and the system exhibited nearly ideal behavior which in view of the near-identity of the polymerization-active groups, is not too surprising (8):



$$CH_2{=}\underset{COOCH_3}{\overset{CH_3}{C}} + CH_2{=}\underset{COO\text{-}PIB\text{-}Ph}{\overset{CH_3}{C}} \xrightarrow{R^\bullet} \underset{\qquad\qquad\qquad\quad PIB\text{-}Ph}{\overset{PIB\text{-}Ph\qquad\qquad\qquad}{\sim\!\sim\!PMMA\!\sim\!\sim}}$$

The Tg of various copolymers showed two transitions: at ∿ -65°C for the PIB segment and another at ∿100°C for the PMMA component indicating substantial phase separation. The solubility characteristics of PMMA-g-PIB copolymers reflect the presence of both constituents in the graft (8). Interestingly, all samples in the 20-40 wt% PIB range were optically clear. The original source should be consulted for further details (9).

An interesting new series of symmetric and/or asymmetric α,ω-diarylpolyisobutylenes have been prepared starting from Ph-PIB-Cl$\overset{t}{-}$:

α,ω-diphenylpolyisobutylene	Ph-PIB-Ph
α-phenyl-ω-tolylpolyisobutylene	Ph-PIB-PhMe
α,ω-ditolylpolyisobutylene	MePh-PIB-PhMe

The syntheses involved quantitative Friedel-Crafts alkylation of benzene and/or toluene by Ph-PIB-Cl$\overset{t}{-}$ or MePh-PIB-Cl$\overset{t}{-}$ (the latter starting material was prepared by the use of p-methylcumyl chloride minifer)(10).

The $\sim CH_2C(CH_3)_2Cl$ end group can be readily dehydrochlorinated to $\sim CH_2C(CH_3){=}CH_2$ which also lends itself to quantitative Friedel-Crafts arylations.

The terminal aromatic rings in the above Ar-PIB-Ar derivatives (where Ar=Ph or PhMe) provided reactive sites for further conversions:

Nitration of Ar-PIB-Ar

$$\text{Ar-PIB-Ar} \xrightarrow[0^{\circ}C]{HNO_3\text{-}H_2SO_4} O_2NAr\text{-PIB-}ArNO_2$$

Reduction of O_2NAr-PIB-$ArNO_2$

$$O_2NAr\text{-PIB-}ArNO_2 \xrightarrow[\substack{\underline{n}\text{-heptane,} \\ \text{reflux}}]{SnCl_2\text{-}HCl} H_2NAr\text{-PIB-}ArNH_2$$

Acryloylation of H_2NAr-PIB-$ArNH_2$ with Acryloyl Chloride

$$H_2NAr\text{-PIB-}ArNH_2 \xrightarrow[\substack{N(CH_2CH_3)_3, \\ THF,\ 0^{\circ}C}]{CH_2{=}CHCOCl} CH_2{=}CHCONHAr\text{-PIB-}ArNHCOCH{=}CH_2$$

Acetylation of Ar-PIB-Ar

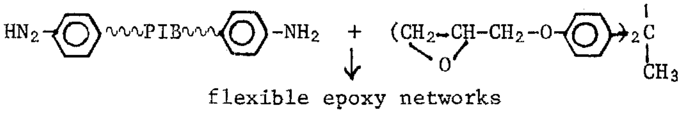
$$\text{Ar-PIB-Ar} \xrightarrow[CS_2,\ \text{reflux}]{CH_3COCl\text{-}AlCl_3} H_3COCAr\text{-PIB-}ArCOCH_3$$

Chlorosulfonation of Ar-PIB-Ar

$$\text{Ar-PIB-Ar} \xrightarrow[0^{\circ}C]{ClSO_3H} ClO_2SAr\text{-PIB-}ArSO_2Cl$$

Scheme II

The quantitative reduction of nitroaryl-telechelic PIB ($\overline{M}_n$ = 12,400) by $SnCl_2$/HCl led to aminoaryl telechelic PIB which was used to cure a readily available bisphenol-A-diglycyl ether (EPON 826):



These epoxy networks exhibited satisfactory mechanical properties (tensile strength ∿2.0 MPa, elongation = ∿700%) and outstanding hydrolytic and thermal stability (no loss of properties after 4 days in 85°C steam or in circulating air oven at 145°C)(10).

SYMMETRIC TELECHELICS

A large amount of information has been assembled during the last few years concerning symmetric telechelics particularly PIB's and poly(β-pinenes)(6) prepared by the inifer technique. The kinetics of the polymerization yielding chlorine-telechelic PIB's have been investigated and some key parameters were determined (11). It has been shown that chain transfer to monomer (an unacceptable side reaction if perfect number average end functionality $\overline{F}_n = 2.0$ is the aim) can be readily avoided by carrying out the polymerization at temperatures below about -30°C (12). Diagnostic proof that chain transfer to monomer is absent (i.e., $C_I = k_{tr,I}/k_p \sim 0$), was provided by Mayo (1/DP versus 1/[M]) plots whose intercepts were zero (12).

In addition to kinetic evidence, a large variety of quantitative structural investigations including infrared, ^{1}H and ^{13}C NMR, and UV spectroscopy combined with double-detector GPC, chlorine end group analyses, etc., have been presented that convincingly demonstrate the symmetric telechelic nature of $\overset{t}{-}$Cl-PIB-Cl$\overset{t}{-}$ (6).

The presence of one single chlorine atom per end group has also been demonstrated by the synthesis of A-B-A triblock copolymers of poly(α-methylstyrene-b-isobutylene-b-α-methylstyrene), PαMeSt-PIB-PαMeSt (13). The synthesis of these materials goes back to the finding that tert.-chlorines in conjunction with alkylaluminum compounds, e.g., Et_2AlCl, readily initiate the cationic polymerization of styrene (St), α-methylstyrene (αMeSt), etc. (5). Thus the scheme of the process leading to the preparation of PαMeSt-PIB-PαMeSt triblock copolymers is as follows (13):

Step 1

$$\text{isobutylene/BCl}_3\text{/pDCC} \longrightarrow \overset{t}{-}\text{Cl-PIB-Cl}\overset{t}{-}$$

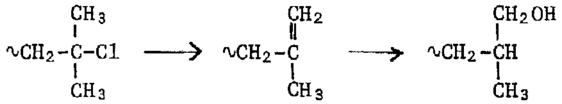
Step 2

$$\overset{t}{-}\text{Cl-PIB-Cl}\overset{t}{-}\text{/}\alpha\text{MeSt/Et}_2\text{AlCl} \longrightarrow \text{P}\alpha\text{MeSt-PIB-P}\alpha\text{MeSt}$$

The overall composition (molecular weight) of these triblocks can be mainly controlled by the concentration of the ingredients. Triblocks comprising of $\overline{M}_n = 10\text{-}20 \times 10^3$ external glassy sequences and $\overline{M}_n = 40\text{-}80 \times 10^3$ central PIB sequences exhibit thermoplastic elastomer character, similar to the well known PSt-polybutadiene-PSt triblocks. Other uses of high molecular weight rubbery chlorine-telechelic PIB's would be as hot melt adhesives)compatibilizing agents.

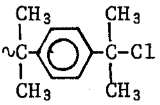
While the high molecular weight telechelic products offer many new potential applications, the low molecular weight (liquid) telechelics are just as promising, particularly when low shear processing is contemplated.

A particularly promising development concerns the synthesis of linear and three-arm star hydroxyl-telechelic PIB's $HOCH_2\text{-}PIB\text{-}CH_2OH$ and $HOCH_2\text{-}\underset{\underset{CH_2OH}{|}}{PIB}\text{-}CH_2OH$, and the polyurethane rubbers obtainable from these liquid prepolymers by reaction with tri- and diisocyanates, respectively. The starting alcohols ($\overline{M}_n$ = 1000-4000) are prepared from the corresponding linear or three-arm star tert.-chloride precursors by quantitative dehydrochlorination followed by hydroboration-oxidation (6,14):

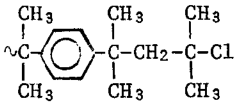


$$\sim CH_2\text{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}Cl \longrightarrow \sim CH_2\text{-}\underset{CH_3}{\overset{CH_2}{\underset{|}{\overset{\|}{C}}}} \longrightarrow \sim CH_2\text{-}\underset{CH_3}{\overset{CH_2OH}{\underset{|}{\overset{|}{CH}}}}$$

Great attention has been devoted to the efficient synthesis of the <u>tert</u>.-chlorine-telechelic starting materials. It has been demonstrated that close to theoretical $\overline{F}_n$ and $\overline{M}_w/\overline{M}_n$ values can be obtained at moderately low temperatures (possibly in refluxing solvent systems) by simple semicontinuous operations (12,15). Indeed it has been recently shown that by continuous constant sufficiently slow addition of isobutylene/inifer feeds into BCl_3 charges readily yields predicted $\overline{F}_n$ and $\overline{M}_w/\overline{M}_n$ values for both linear and three-arm star precursors (15). In contrast, the conventional polymerization technique of adding the BCl_3 coinitiator to monomer/inifer charges may yield broader than expected or multimodal molecular weight distributions, and the products may contain "unfired" or "once-fired" end groups (15,16):

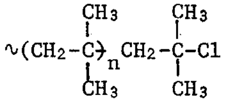


unfired end group



once-fired end group

While the presence of these end groups does not change the value of $\overline{F}_n$, the reactivity of these termini is somewhat different from the aliphatic tert.-chloro terminus of PIB:



$$\sim(CH_2-\underset{CH_3}{\overset{CH_3}{C}})_n CH_2-\underset{CH_3}{\overset{CH_3}{C}}-Cl$$

The reason why conventional techniques may produce less well-defined products and the semicontinuous process yields virtually theoretical telechelics is that in the former process monomer and inifer concentrations continuously decrease during a run, whereas these parameters remain essentially constant in the semicontinuous process (15).

POLYISOBUTYLENE-BASED POLYURETHANE NETWORKS

The linear or three-arm star hydroxyl-telechelic PIB's are useful starting materials in conjunction with tri- or diisocyanates for the preparation of model polyurethane networks (17). Beyond the scientific significance of these model networks (i.e., networks which do not contain dangling ends and whose $\overline{M}_c$ is uniform and equal to the $\overline{M}_n$ of the rubbery PIB starting material for exploring details of the new rubber elasticity theory (18), these new polyurethanes show a useful combination of physical-chemical properties (17).

A series of experiments have been carried out with three-arm star hydroxyl-telechelic PIB's of $\overline{M}_n$ = 3,100-21,000. Stoichiometric amounts of these materials were reacted with 4,4'-diphenylmethane diisocyanate (MDI) and the networks so obtained were characterized by swelling, modulus, and extraction measurements. According to

Table 1

Hot Water and Hot Air Resistance of PIB-based Polyurethanes

	Before Degradation Testing		After Exposure To Hot Water^b			After Air-Oven Aging^c		
$\overline{M}_c{}^a$	$\sigma_{t,b}$(Pa)	E_b(%)	$\sigma_{t,b}$(Pa)	E_b(%)	Change in $\sigma_{t,b}$(%)	$\sigma_{t,b}$(Pa)	E_b(%)	Change in $\sigma_{t,b}$(%)
2,100	1.85×10^7	227	1.76×10^7	222	4.86	1.81×10^7	224	2.16
3,700	1.81×10^7	300	1.73×10^7	298	4.42	1.76×10^7	290	2.76
7,700	9.40×10^6	510	9.34×10^6	492	0.64	9.11×10^6	494	3.09

a) Swelling in n-pentane

b) ASTM-D3137

c) ASTM-D537

the data obtained the products can indeed be regarded to be model networks ($\overline{M}_c = \overline{M}_n$, negligible extractables) (17).

The tensile stress, modulus and elongation of the products were determined; subsequently the networks were subjected to the action of steam (ASTM D-3137) and circulating hot air (ASTM D-537), and then the above properties were again determined. According to the data shown in Table 1 the dynamic mechanical properties of the networks were essentially unaffected by the rather aggressive ASTM tests used.

Evidently, the hydrolytic and thermal stability of PIB-based polyurethane networks is outstanding.

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