

Synthesis of Telechelic Dithiol Oligomers Containing Sulfur Atoms-Moisture Barrier Properties

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SYNOPSIS

The aim of this work was to synthesize new polysulfide materials from butadiene, styrene, isoprene, and methacrylate monomers and to study their moisture vapor permeability. For this purpose, a series of telechelic dithiol polysulfide oligomers were prepared by a polycondensation reaction between dianionic species of the corresponding monomer and sulfur or by reduction of the resulting cyclic polysulfide polymers. This last process was followed by ¹H-NMR and elemental analysis. It was established that the scission of the polysulfide linkages to thiol end groups was fastest with the greatest number of sequential sulfur atoms. The thiol reactivity was used to prepare cured materials from the liquid oligomers and manganese dioxide: Networks were obtained from butadiene dithiol oligomers, whereas chain extension occurred for the others. Infrared analysis suggests that the reticulation reaction results from thiol addition to the double bond. The moisture vapor transmission test applied to these different materials showed that these new compounds present good moisture barrier properties.

INTRODUCTION

Liquid polysulfide polymers have reached universal acceptance as high-performance polymers in the aircraft industry for their fuel resistance and in the construction industry for their excellent adhesion and UV resistance as insulating glass sealants. In this last application, water condensation between the two glass plates has to be avoided because in such an enclosed atmosphere glass attack may occur, leading to white depositions of sodium carbonate. Generally, a polyisobutylene sealant or a spacer containing molecular sieves prevent water migration; the polysulfide sealant that slows down moisture transmission gives principally the mechanical cohesion of the two pans. To improve the moisture barrier property of this sealant, we decided to synthesize new polysulfide dithiol polymers since water permeability is mainly controlled by the chemical structure of the polymer.¹ Generally, polymers containing thiol groups are obtained by polymerization

of thiol-containing monomers² or by chemical modification of preformed polymers.³⁻⁶ This last process is often used in the industry. Thus, the reduction of the sulfur bridges of polysulfide polymers was developed by Thiokol Corporation.⁷ Products Research Corporation has commercialized liquid polymers that have been functionalized by addition of dithiol to terminal unsaturations.⁸ In our laboratory, a new synthesis of polysulfide polymers has been investigated, from vinylic or dienic monomers, sodium, and elemental sulfur.^{9,10} Depending upon the experimental conditions and chemical monomer nature, liquid dithiol oligomers or cyclic polysulfide polymers have been obtained. In this last case, telechelic thiol polymers have been prepared by submitting the cyclic compounds to a hydrogenation reaction. This paper reports the synthesis and determination of the water permeability of the cured materials.

EXPERIMENTAL

Synthesis of Cyclic Polysulfide Polymers

Polysoprene Polysulfide (Run 1, Table I)

In a glass reactor placed under argon, 1 L of THF and 0.38 mol of sodium were introduced. After low-

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Table I Functionality of Polysulfide Polymers Prepared for Different Values of $K = [\text{Carbanions Formed}]/[\text{S}_8]$

Monomer	Run	$K < 2$			$K > 2$			
		n	%SH _{exp}	%SH _{theo}	Run	n	%SH _{exp}	%SH _{theo}
Isoprene	1	2.1	0.45	7	4	2.5	17.8	18.3
Butadiene	2	3.6	0.05	0.8	5	10.1	0.1	0.8
Styrene	3	17.6	0.1	0.67	6	39	0	0.1

ering the temperature to -40°C , sulfur (0.13M) and isoprene (0.21M) were added successively. The solution was stirred for 4 h before filtering and poured into an aqueous acidic solution. After addition of diethylether, the organic layer was washed with water and dried over magnesium sulfate. The dithiol oligomer was isolated after filtration and evaporation.

ANAL: S, 35.3%; $\bar{M}_n = 930$.

The same procedure was applied to the other monomers:

Polybutadiene Polysulfide (Run 2, Table I)

[M] = 0.8M [Na] = 0.8M [S₈] = 0.26M. ANAL: S, 30%, $\bar{M}_n = 8000$.

Polystyrene Polysulfide (Run 3, Table I)

[M] = 0.8M [Na] = 0.55M [S₈] = 0.06M. ANAL: S, 10.5%, $\bar{M}_n = 9800$.

Synthesis of Dithiol Oligomers

I. One Pot Process

This was the same procedure as above with the following reactant concentrations:

Isoprene (Run 4, Table I)

[M] = 0.74M, [Na] = 0.52M, [S₈] = 0.06M. ANAL: S, 21%, $\bar{M}_n = 360$.

Butadiene (Run 5, Table I)

[M] = 0.8M, [Na] = 0.56M, [S₈] = 0.06M. ANAL: S, 11%; $\bar{M}_n = 8000$.

Styrene (Run 6, Table I)

[M] = 0.8M, [Na] = 0.52M, [S₈] = 0.03M. ANAL: S, 2.8%; $\bar{M}_n = 54,000$.

II. Reduction of Polysulfide Polymers

General Procedure. Fifteen mL of concentrated hydrochloric acid were added dropwise under constant stirring into a 250 mL flask containing 5 g of zinc powder, a solvent mixture (100 mL of benzene and 50 mL of isopropanol) and 10 g of polybutadiene polysulfide polymer (S, 22%). After 2 h, the stirring was stopped and a phase separation occurred. The upper layer was dried over sodium sulfate and filtered. The dithiol oligomer was isolated by evaporation of the solvent under vacuum.

ANAL: C, 74.6%, H, 9.3%, S, 16.0%, SH, 11.3%.

¹H-NMR Study of the Polybutadiene Polysulfide Reduction. The total amount of reagents was added in five equivalent aliquots at 2 h intervals. After each 2 h reaction time, the resulting polymers were isolated and analyzed by ¹H-NMR.

Networks

Cured polymers were prepared by condensation of thiol groups using active-grade manganese dioxide (Shepperd).

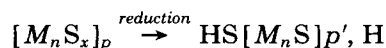
Characterization of Polymers and Oligomers

The elemental analysis was carried out with a Carlo Erba elemental analyzer model 1106. The thiol content was determined by complexation of the thiol group with a silver nitrate solution and titration of the excess silver with a silver electrode.

The amount of cross-linking was measured by extraction of soluble material in refluxing tetrahy-

drofuran with a soxhlet extractor over a 24 h period. The $^1\text{H-NMR}$ spectra were recorded on a Hitachi Perkin-Elmer R24A (60 MHz) spectrometer using carbon tetrachloride as the solvent. The IR spectra were recorded with a Perkin-Elmer 800 spectrophotometer.

Determination of the Degree of Polycondensation after Reduction: p'



p' can be evaluated from the ratio %SH/%S:

$$\%S = \frac{(p' + 1)S}{(p' + 1)S + p'nM + 2H} \quad (\text{I})$$

$$\%SH = \frac{2(S + H)}{(p' + 1)S + p'nM + 2H} \quad (\text{II})$$

where S: atomic weight of sulfur, M: atomic weight of monomer, and H: atomic weight of hydrogen. Thus,

$$\frac{\%SH}{\%S} = \frac{2(S + H)}{p' + 1} \quad \text{and}$$

$$p' = \frac{2(S + H)(\%S - \%SH)}{S(\%SH)} = \frac{66(\%S - \%SH)}{32\%SH}$$

Determination of the Organic Chain Length: n

From p' and one of the previous formulas (I or II), n can be calculated:

$$n = \frac{S(p' + 1)}{\%S \cdot p' \cdot M} - \frac{2H}{p' \cdot M} - \frac{(p' + 1)S}{p' \cdot M}$$

Before reduction, n can be evaluated from the sodium and monomer consumptions: $n = 2[M]/[Na]$. In the case of polybutadiene polysulfide, n can be also determined from NMR and the sulfur content.¹⁰

Determination of the Sulfur Rank (x) before Reduction

During the reduction reaction, the organic chain length is not modified and, consequently, the sulfur rank x before reduction can be evaluated:

$$\%S = \frac{xS}{xS + nM}, \quad \text{therefore } x = \frac{n \cdot M \cdot \%S}{S(1 - \%S)}$$

Determination of the Molecular Weight

The molecular weight of the polymers and oligomers was determined by gel permeation chromatography and vapor-phase osmometry.

Determination of the Moisture Vapor Transmission: MVT

A container, half-full of water, was covered by a membrane of polymer and placed in a dessicator containing phosphorous pentoxide. The water flow through the polymer was measured by weighting the container at regular intervals. From the slope of the curve, weight loss vs. time, the MVT (in $\text{g m}^{-2} \text{day}^{-1} \text{cm}$) was calculated:

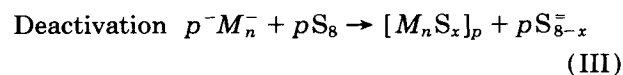
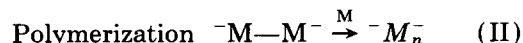
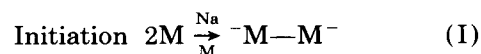
$$\text{MVT} = 24(\Delta M / \Delta t) \cdot e/a$$

where ΔM = weight loss in grams; Δt = time corresponding to ΔM in hours; a = membrane surface in m^2 ; e = membrane thickness in cm.

RESULTS AND DISCUSSION

Synthesis of α,ω Dithiol Oligomers

The synthesis of α,ω dithiol oligomers was first investigated from the one-pot process developed in our laboratory. This latter consists of mixing in a polar solvent (THF) the monomer, sulfur, and sodium. The overall process can be summarized by the following reactions:



When the reaction was carried out in a large excess of elemental sulfur ($K = [\text{carbanions formed}]/[S_8] \leq 2$), the polymers obtained were principally cyclic.⁹ To favor the splitting of the sulfur bridges and, consequently, the thiol formation, it was necessary to carry out the synthesis in sulfur deficit.¹⁰ Under this condition, the carbanions formed attack the sulfur linkages (step IV). Several experiments have been done, and the characteristics of the resulting polymers are summarized in Table I. It can be observed that the functionalization in thiol depends greatly on the monomer used. For styrene and butadiene, the organic chain length (n) between two

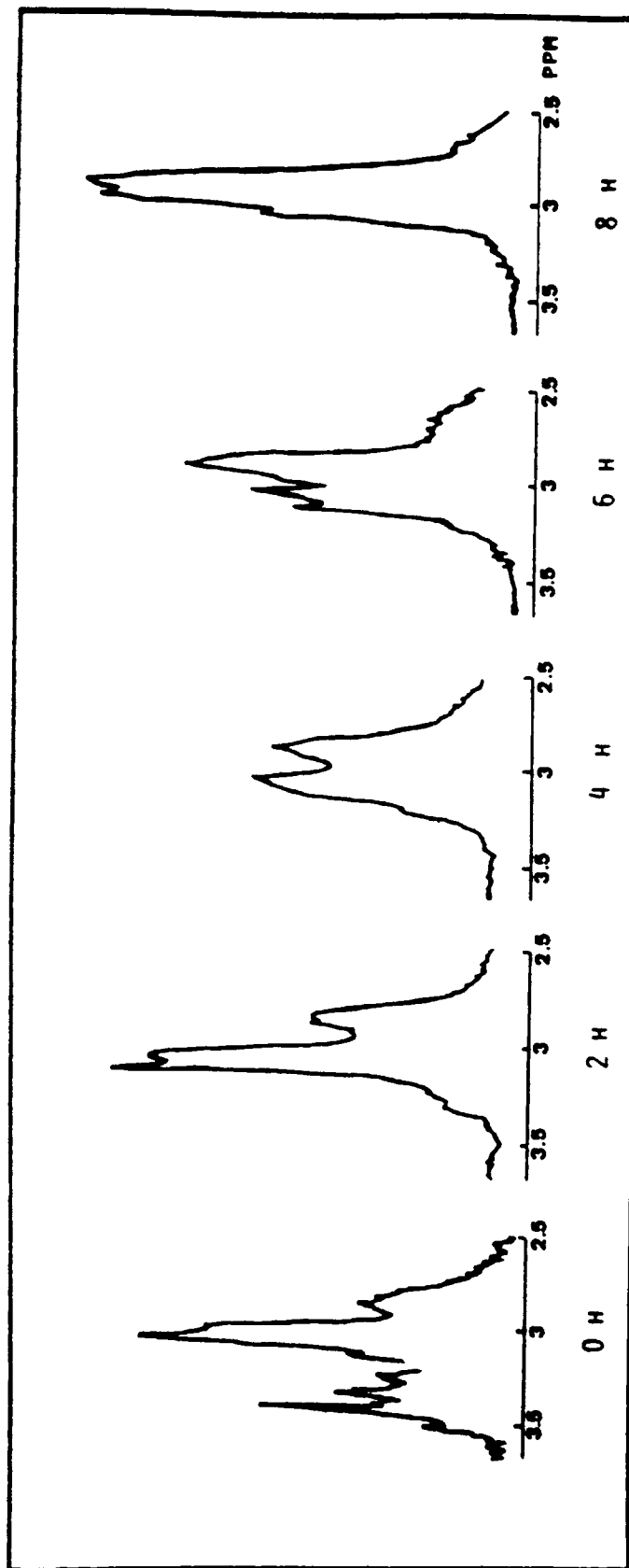
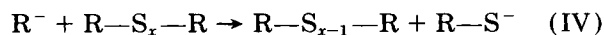


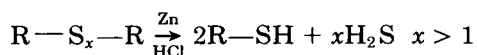
Figure 1 Evolution of the proton chemical shift of the carbon-bearing sulfur atoms during the reduction reaction of polybutadiene polysulfide.

sulfur bridges increases sharply when K becomes higher than two, and the thiol content is far from the theoretical value. This behavior can be explained as follows: When sulfur is totally consumed ($K > 2$), the carbanions formed can add new monomer molecules (step II) or react with the sulfur bridges of the polymer chain (step IV):



If this last reaction is less favored than the previous deactivation reaction on S_8 (step III), propagation occurred to a larger extent. This is what was observed with styrene and butadiene as monomers. In the case of isoprene, both deactivation reactions are of the same order of magnitude and the chain length (n) remains unchanged; consequently, the splitting of the sulfur bridges occurs, leading to a high yield of the thiol group.

To get dithiol oligomers for the different monomers, a new route has been studied, based on the reduction reaction of the cyclic polysulfide polymers. Two methods have been attempted: addition of lithium aluminum hydride or reaction with "nascent hydrogen" (Clemmensen reaction). The best results have been obtained with the last method as it has been observed by Weinstein and co-workers for other polysulfide polymers.⁴ This reduction process is based on the following reaction:



To get more information about this reduction reaction, the evolution of the sulfur linkages has been

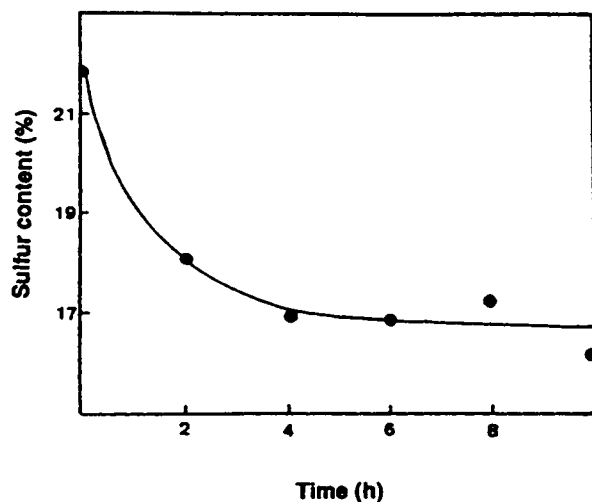


Figure 2 Variation of the sulfur content with time in polybutadiene polysulfide during the reduction reaction.

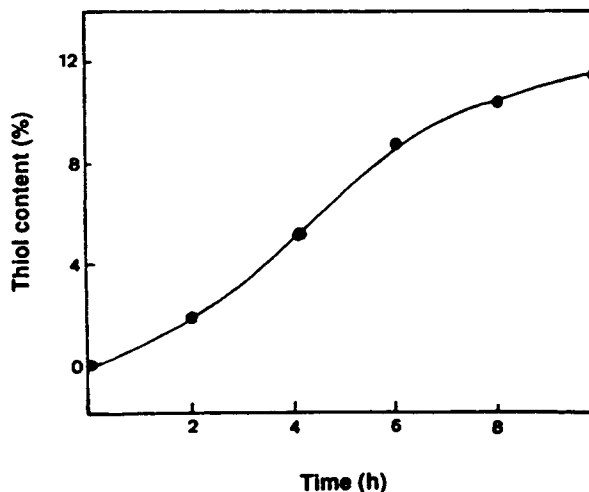
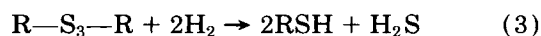
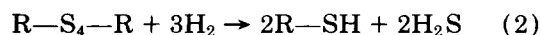
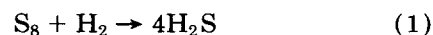


Figure 3 Variation of the thiol content with time in polybutadiene polysulfide during the reduction reaction.

followed by 1H -NMR in the case of polybutadiene polysulfide. As we have shown in a previous study,¹⁰ the chemical shifts of the protons on the adjacent carbon atom linked to sulfur atoms depend of the sulfur rank of the bridge:

- 2.9 ppm: H on the carbon bearing one sulfur atom
- 3.1 ppm: H on the carbon bearing two sulfur atoms
- 3.4 ppm: H on the carbon bearing three to four sulfur atoms

In Figure 1, the proton peaks corresponding to tetra and trisulfide bridges disappear first; this is followed by a decrease of the disulfide peak while the intensity of the monosulfide peak increases, showing thiol formation. This fact is confirmed by the variation of sulfur and thiol contents (Figs. 2 and 3): At the beginning (0–4 h reaction time), the sulfur content decreases rapidly and remains constant. At the same time, the thiol yield increases regularly. All these data can be summarized by reactions (1)–(4):



The loss of sulfur at the beginning of the reduction is a result of hydrogen sulfide formation from free sulfur dissolved in the original polymer and from the tetra and trisulfide linkages. The thiol function

Table II Characteristics of Dithiols Oligomers HS—[M_nS]_p—H

Run	Polymer	Before Reduction			After Reduction						
		\bar{M}_n	%S	<i>n</i>	\bar{M}_n	%S	%SH _{exp}	%SH _{theo}	<i>p</i> '	<i>n</i>	<i>x</i> _{init}
7	PBuS	3,000	30	2.3	550	22	12.0	12.0	2.7	2.8	2.0
8	PBuS	8,000	11	10.1	800	9	8.3	8.25	1.3	10.5	2.2
9	PBuS	8,000	21	5.4	600	15	10.9	11.0	1.8	5.2	2.3
10	PBuS	9,000	22	4.6	580	16	11.3	11.4	2.1	4.3	2.0
11 ^a	PBuS	9,000	22		1300	17	4.9				
12 ^a	PBuS	9,000	22		4100	18	1.6				
13	PIsS	1,700	19		770	13	8.6	8.6	2.1	3.7	1.5
14	PStyS	2,000	22		430	17	15.3	15.3	1.3	3.7	1.8
15	PMMAS	600	35		400	17	16.6	16.5	1.1	2.1	1.9

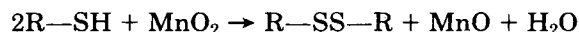
^a Partial reduction: 20% (run 11) and 10% (run 12) of the total amount of zinc necessary for the total reduction.

is obtained from sulfur bridges containing two to four sulfur atoms.

By this method, various telechelic polysulfide polymers have been prepared (Table II). A good correlation was observed between the thiol analysis and the theoretical amount calculated from molecular weight. Concerning the organic chain length (*n*) between two sulfur bridges, elemental analysis and ¹H-NMR are in good agreement. In some cases (runs 11 and 12), the molecular weight has been adjusted by a partial reduction of the polysulfide linkages.

Curing of Dithiol Polysulfide Polymers

The transformation of liquid oligomers in handling membrane has been done by using the reactivity of the thiol function toward the oxidizing agent.¹² In the presence of manganese dioxide, a coupling reaction occurs between the thiol groups, leading to the formation of a disulfide bridge. This reaction is used in organic chemistry¹³ to synthesize disulfide:

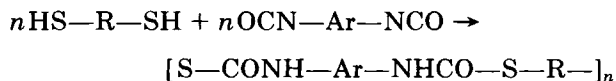


When this reaction was applied to our polymers, cross-linking appeared for polybutadiene polysulfide, while chain extension was observed for the others (Table III). The first observation suggested two hypotheses:

- The presence of a functionality per chain greater than two, due to hydrogen sulfide addition to double bond during reduction.

- A thiol addition on unsaturation during the curing process.

The first hypothesis is less probable because the reaction generally requires the presence of catalyst or high temperature.¹⁴ Nevertheless, the functionality of the reduced samples has been checked by reacting the SH group with a diisocyanate in a stoichiometric amount:

**Table III** Action of Manganese Dioxide on Dithiol Oligomers (Temperature: 80°C, Time: 6 h)

Polymers	%S	%SH	\bar{M}_n	After Curing	
				% Cross-linked	\bar{M}_n
PBuS	22	12.2	550	72	
PBuS	9	8.3	800	61	
PBuS	15	10.9	600	75	
PBuS	16	11.3	580	83	
PIsS	21	17.6	360	0	3500
PStyS	17	15.3	430	0	2500
PStyS 50%	17	15.3	430	56	
PBuS 50%	15	10.9	600		
PMMAS	17	16.6	400	0	2000
PMMAS 50%	17	16.6	400	80	
PBuS 50%	15	10.9	600		

Table IV Principal Absorbance Bands of PBuS and PIsS in Infrared

Vibration	PBuS Frequency (cm ⁻¹)	PIsS Frequency (cm ⁻¹)
*CH stretching =CH, =CH ₂	3,074	3,069
CH ₂ , CH	2,971	2,963
*SH stretching	2,550	2,569
*C=C stretching	1,638	1,639
*CH ₂ deformation	1,439	1,446
*CH of 1-2 and 1-4 cis structure in plan deformation	1,417	1,412
*CH ₃ deformation		1,373
*CH of 1-2 structure out-of-plan deformation	995	910
*CH of 3-4 structure		890
*CH of 1-4 structure out-of-plan deformation	966	850

In all cases, a molecular weight increase was obtained without any cross-linking. This result shows that the reticulation observed in the case of polybutadiene polysulfide cannot be related to a functionality greater than two.

Concerning the second hypothesis, the addition of a thiol group on unsaturation is well known and generally occurs in the presence of radical¹⁵ or acid catalyst.¹⁶ To confirm this possibility, the cross-linking reaction has been studied by infrared spectroscopy. In Table IV, the principal IR absorptions of a polysulfide polybutadiene dithiol are presented. The SH stretching vibration at 2550 cm⁻¹ is weak

but very useful in this study because the presence of a band in this region gives decisive evidence for the occurrence of a thiol group. As manganese dioxide absorbs in IR, the curing process was done at 100°C without an oxidizing agent. Under these conditions, a reaction time of 12 h was necessary in order to obtain a cross-linked material (Table V). In the same time, the other polysulfide polymers presented no molecular weight change, and in the case of dithiol polysulfide polyisoprene, the SH absorption at 2559 cm⁻¹ remained unchanged. The examination of the IR spectrum of the cured polybutadiene polysulfide (Fig. 4) shows a decrease of the SH stretching vibration with a slight variation of the intensity of the band at 1638 cm⁻¹. This addition reaction occurs principally on the 1-2 structure as it can be observed by the lowering of the absorption at 995 cm⁻¹. This result can be related to a better mobility and accessibility of this unsaturation as a pendent group and can explain the nonreactivity of the polyisoprene chain (low content of 1-2 structure, lower than 10%).

From these data, different cross-linked polymers have been prepared by curing mixtures of dithiol polybutadiene and saturated dithiol oligomers. Sequences of polymethacrylate or polystyrene have been incorporated into the network (Table III). ¹H-NMR spectra done on extractable products confirm that more than 50% of the saturated dithiols oligomers have produced chain extension.

Moisture Barrier Properties

The properties of the moisture barrier have been evaluated by measuring the moisture transmission rate through membrane presenting the same thickness (0.1 cm). The data collected in Table VI show

Table V Effect of Temperature on Dithiol Oligomers

Polymer	From Synthesis	%S	%SH	\bar{M}_n	% Cross-linked
PBuS ^a	7	9	8.3	800	61
PBuS ^a	9	15	10.9	600	94
PIsS ^a	4	21	17.8	360	0
PMMAS ^a	15	17	16.6	400	0
PStyS ^a	14	17	15.3	430	0
PBuS ^b	11	17	4.9	1,300	90
PBuS ^b	12	18	1.6	4,100	53

^a Heating 12 h at 100°C.

^b 96 h at 20°.

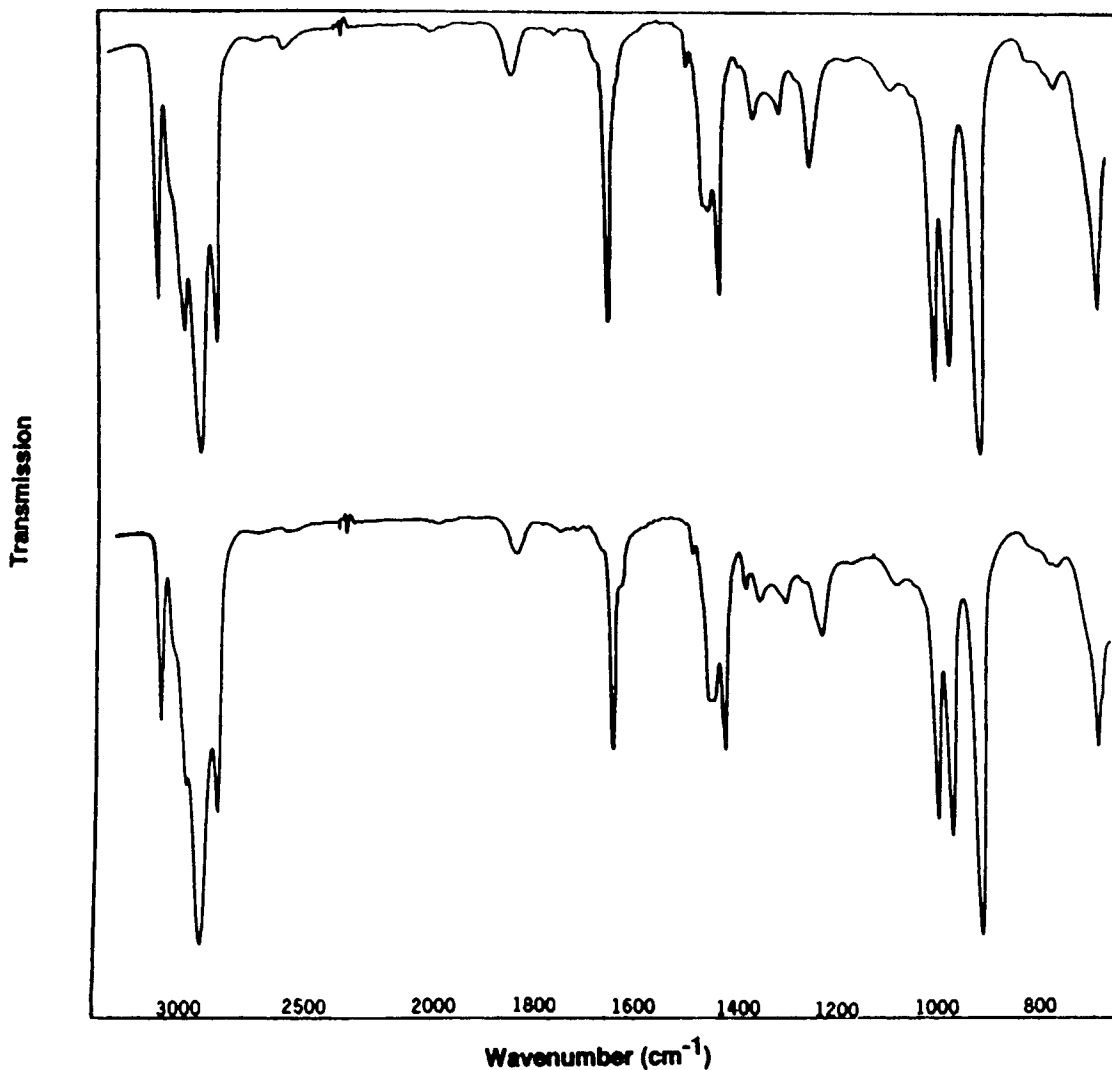


Figure 4 Evolution of the infrared spectra of dithiol polybutadiene polysulfide during curing at 100°C: $t = 0$ h, upper spectrum; $t = 12$ h, lower spectrum.

that industrial polymers, used as insulating glass sealant, present higher MVT values than do the other polymers. The difference is more pronounced when no filler (CaCO_3) is added: 2.9 for Thiokol or 5.7 for permapol compared to 0.61 in the worst case of polybutadiene polysulfide material. The addition of CaCO_3 leads to contradictory results as MVT values decrease for Permapol and polybutadiene polysulfide (0.61 \rightarrow 0.18) and remain unchanged on Thiokol (2.9 \rightarrow 3.1). This behavior can be related to a difference of compatibility between the filler and the polymer chain.¹⁷ It seems that a better compatibility between the calcium carbonate and the P BuS gives a higher cohesive-energy to the polymer that diminishes the diffusion coefficient (D). How-

ever, the permeability constant depends on D but also on the vapor solubility constant S ($P = D \cdot S$). The data show that calcium carbonate does not favor the water solubility since P decreases or remains constant.

A slight improvement of the permeability is also observed when polystyrene chains are present in the membrane (Table VII). The MVT values vary between 0.37 and 0.12 for polystyrene contents between 0 and 50%. This can be related to an increase of the stiffness of the material. Generally, the diffusion coefficient is higher for an elastomeric compound than for a rigid one due to the possibility for elastic chain to create "holes" that enhance the diffusion process of water through the material. As it

Table VI Influence of the Chemical Nature of the Polymer and of the Presence of CaCO₃ on the Moisture Vapor Transmission

Samples	Polymer	%S in Polymer	% 1.4 Unsaturation	MVT (g day ⁻¹ m ⁻² cm)
1	PBuS	9	33	0.61
2	PBuS 50% CaCO ₃ 50%	9	33	0.18
3	PBuS	15	50	0.28
4	PBuS 50% CaCO ₃ 50%	15	50	0.24
5	PBuS	15	84	0.37
6	Thiokol	HS—[CH ₂ CH ₂ OCH ₂ OCH ₂ CH ₂ S ₂] _n —SH		2.90
7	Thiokol 50% CaCO ₃ 50%			3.10
8	Permapol P2	HS—[CH ₂ —CH(CH ₃)—O] _n —CH ₂ CH(CH ₃)—SH		5.70
9	Permapol 50% CaCO ₃ 50%			1.55

can be observed in runs 10–12, the effect of sulfur atoms on water transmission is negligible. The MVT is equal to 0.30–0.45 for samples containing 21 to 16% of sulfur. The same conclusion can be drawn concerning the influence of the microstructure of the polybutadiene. In fact, the variations observed did not follow a consistent pattern (runs 1, 3, and 5), but the small differences between the MVT values indicate that the microstructure effect on permeability is negligible.

CONCLUSION

From a new process of polysulfide polymer synthesis, different dithiol oligomers have been prepared. The

study of this one-pot process has shown that functional oligomers can be obtained in the case of isoprene when the reaction is done in sulfur default. For the other monomers, the problem has been solved by submitting the corresponding polysulfide polymers to a reduction reaction.

By curing the oligomers in the presence of manganese dioxide, a cross-linking reaction has been observed in the case of polybutadiene, due to thiol addition on double bond. This reaction has been used to prepare membranes from which water permeability studies have been done. The results have shown that these new polymers present better moisture impermeability properties than that of the polysulfide polymers currently used in insulating glass.

Table VII Influence of the Sulfur Content and of PSty or PMMA Sequences on the Moisture Vapor Transmission

Samples	Polymer	%S in Polymer	% 1.4 Unsaturation	MVT (g day ⁻¹ m ⁻² cm)
10	PBuS	16	52	0.45
11	PBuS	18	52	0.46
12	PBuS	21	52	0.30
13	PBuS	15	84	0.37
14	PBuS 75% PStyS 25%	11		0.18
15	PBuS 50% PStyS 50%	12		0.12
16	PBuS 50% PMMAS 50%	8		0.34

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