Detection of a New Crosslinking and Properties of Liquid Polysulfide Polymer

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ABSTRACT: Polysulfide polymer was found in the 19th century. At present, this polymer consists of the repetition of disulfide linkage and diethyl formal and has SH terminals. This liquid polymer (LP) is cured by lead dioxide. We studied polysulfide polymerization and elastomeric mechanical properties of cured LP. The condition of polymerization greatly influenced its elastomeric mechanical properties. These phenomena could not be explained from the point of residual unreacted chlorine or produced OH terminals. We found that additional crosslinking sites are produced during polymerization besides crosslinking agents trichloropropane (TCP) by using the Insensitive Nuclei Enhanced by Polarization Transfer (INEPT) method. We proposed their chemical structures and reaction scheme of their formation. TCP and also these additional crosslinking sites influence the modulus of cured LP. The sum of the intensity of their crosslinking sites by ¹³C-NMR had good correlation with 300% modulus of cured LP. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 59–66, 1999

Key words: polysulfide polymer; crosslinking; polymerization; ¹³C-NMR INEPT method; elastomeric sealant

INTRODUCTION

In 1840, Lowig discovered that an elastic material was produced when ethylene dichloride was reacted with potassium polysulfide.¹ Eighty-five years after this discovery, Patrick² started investigating rubbery elastic substances synthesized by treating 1,2-dichloroethane with sodium polysulfide caustic solution and established the backbone of polysulfide polymer. Many dichloro compounds were investigated as monomers for polysulfide formation. The dichloro monomer of the greatest utility was found to be bis(2-chloroethyl)formal (IG-Farben, Germany) because the yield was usually very high and its polymer had very low odor and showed high flexibility even at low temperatures.^{1,3} In most cases, a small quan-

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tity of 1,2,3-trichloropropane (TCP) was used in combination with this dichloro monomer, the function of which was the introduction of branches in the polysulfide polymer chains. Branched structures can afford excellent elastomeric networks. Finally, Patrick and Ferguson² found the reduction cleavage of relatively high molecular weight polysulfide polymer into low molecular weight; this low molecular liquid polymer is at present the main polysulfide polymer.

Polysulfide polymer is produced by polymerization of sodium polysulfide ($Na_2S_x : x = 2.0-2.3$) and bifunctional organic compounds (i.e., bis(2chloroethyl)formal), usually with a small amount of trifunctional branching agent (e.g., TCP).

$$\begin{split} n(\text{CIRCl} + \text{Na}_2\text{S}_x) &\to \sim (\text{RS}_x)_n \\ &\sim + 2n\text{NaCl} \quad \text{R}: \text{CH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2 \end{split}$$

Experimentally, high molecular weight polymers are obtained when the mol ratio of dichlo-

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Sample	TCP (mol %)	x in Ma_2S_x	Viscosity (poise)	MW	300% Modulus (MPa)	Tensile (MPa)	Elongation (%)
А	0.0	2.25	450	4000	1.0	1.7	950
В	0.2	2.25	450	4000	1.1	2.1	1100
С	0.5	2.05	450	4000	1.0	2.0	1200
D	0.5	2.25	450	4000	1.4	2.4	950
E	1.0	1.85	450	4000	0.8	1.6	1300
F	2.0	2.25	450	4000	2.4	3.2	650

Table I Typical Physical Properties of Tested LP

roalkane to sodium polysulfide is substantially smaller than unity. This deviation from the stoichiometry results from the presence of hydrolysis of dichloro monomer to monochloro hydroxy alkane (HORCl) during the polymerization, which terminates further condensation of the chain by forming inert hydroxy groups.

$$\sim S_x RS_x Na + CIROH \rightarrow \sim S_x RS_x ROH + NaCl$$

The role of excess sodium polysulfide is the removal of this inert terminal into the aqueous phase according to the "toughening" theory.³

$$\sim S_x RSSROH + NaSSNa \rightarrow$$

 $\sim S_x RSSNa + NaSSROH$ (1)

The obtained polymer dispersion was washed by hot water followed by decantation. The diameter of the particle in this dispersion was about 10 μ m. Molecular weight of the polymer forming this particle was about 200 × 10³. Sodium sulfite and sodium hydrosulfide were added to the clean dispersion. In this process, the polysulfide polymer was reduced to disulfide and some disulfide was cleaved to SH terminals.

$$\sim \text{ RSSSR} \sim + \text{ Na}_2 \text{SO}_3 \rightarrow \\ \sim \text{RSSR} \sim + \text{ Na}_2 \text{S}_2 \text{O}_3 \quad (2)$$

$$\sim$$
 RSSR \sim + NaSH \rightarrow

$$\sim$$
 RSSNa + HSR \sim (3)

$$\sim \text{RSSNa} + \text{Na}_2\text{SO}_3 \rightarrow$$

 $\sim \text{RSNa} + \text{Na}_2\text{S}_2\text{O}_3$ (4)

Finally, these polymers were neutralized with acids, then washed and dried. Their molecular weight was between 1000 and 8000.

Such liquid polysulfide polymers (LP), which were discovered by Patrick and Ferguson,² are now well known in the polymer industry. SH groups are at their chain ends and disulfides are in their main chains. These liquid polymers are oxidized by oxidizing agents (e.g., lead dioxide or manganese dioxide), resulting in polymer network structures. These metallic curing agents rapidly convert the SH

Sample	TCP (mol %)	300% Modulus (MPa)	Peak No. of Tertiary Carbon					
			(1)	(2)	(3)	(4)	(5)	
А								
LM^{a}	0.0	0.31	0.00	0.00	0.18	0.35	0.06	
$\mathbf{M}\mathbf{M}$	0.0	0.85	0.00	0.00	0.16	0.46	0.06	
$\mathbf{H}\mathbf{M}$	0.0	1.50	0.00	0.00	0.18	0.55	0.09	
В	0.2	1.03	0.04	0.00	0.20	0.42	0.11	
С	0.5	0.95	0.07	0.05	0.33	0.34	0.08	
D	0.5	1.43	0.13	0.04	0.22	0.38	0.11	
Е	1.0	0.80	0.11	0.15	0.41	0.20	0.07	
F	2.0	2.34	0.20	0.12	0.57	0.38	0.08	

Table II Amount of Tertiary Carbon and 300% Modulus of Different LP

^a LM, toughening period is 1 h; MM, toughening period is 2 h; HM, toughening period is 3 h.

Base compound Curing paste	LP SRF carbon black PbO ₂ Chlorinated paraffin Stearic acid Alumina	100 part 30 part 7.5 part 5.0 part 0.2 part 0.2 part
	Alumina	0.2 part

Table III Formulation of Curing System of LP

terminals to SS linkage at room temperature and the liquid polymer becomes elastomeric.

$$\begin{split} \mathrm{HSR} &\sim \sim \mathrm{RSH} + \mathrm{PbO}_2 \rightarrow \\ &\sim \sim \mathrm{RSSR} \sim \sim + \mathrm{PbO} + \frac{1}{2}\mathrm{H}_2\mathrm{O} \end{split}$$

$$\begin{split} HSR \sim &\sim RSH + \, MnO_2 \rightarrow \\ &\sim \sim RSSR \sim \sim + \, MnO + \frac{1}{2}H_2O \end{split}$$

Main applications of LP include building sealant, aircraft sealant, and insulating glass sealant, due to their specific characteristics (i.e., oil resistance, gas barrier, and good weatherproofing properties). In the building sealant, joint movement of spaces between curtain walls in high-rise buildings is more than $\pm 50\%$ in winter and summer or daytime and midnight. Figure of the stress–strain (SS) curve of cured LP is similar even if cured LP's modulus changes. So we represent cured LP's 300% modulus (modulus at 300% elongation) as modulus of elasticity in the next section, because its value is easy to determine by



Figure 1 Dissipation rate of chlorine in LP (ppm) at 112° C.



Figure 2 OH in LP during polymerization at 112°C.

tensile meter and has actual meaning in the building sealant to follow the movement.

Mechanical properties of cured LP are determined by the conditions of polymerization. One important factor of determining modulus is the amount of trifunctional branching agents (TCP) introduced during polymerization. Also, the modulus of cured LP depends on the toughening temperature and the toughening time. According to the "toughening" theory³ represented by eq. (1), OH terminals of its polymer decrease and its molecular weight increases during the polymerization in



Figure 3 300% Modulus of cured LP during polymerization at 112° C.



Figure 4 Residual SH of cured LP by FTIR.

which the amount of sodium polysulfide is in excess. We measured the amount of OH and Cl terminals of the polymer during polymerization and studied any crosslinkings other than that introduced by TCP. The crosslinking sites from TCP that are tertiary carbons in LP could be measured by ¹³C-NMR and the INEPT method.⁴ Mazurek and Moritz studied ¹³C-NMR of LP and identified some crosslinking sites assigned to TCP.⁵ We found that there are some tertiary carbons not assignable to TCP being produced during polymerization. These results are important in considering physical properties of elastomeric LPs.

EXPERIMENTAL

Materials

Molecular weight and SH of polysulfide polymers that were produced and employed in this study had about 4000 and $\sim 1.6-1.9$ wt %. Their viscosity was about 45 Pa · s at 25°C. Representative condition and physical properties of these materials are shown in Tables I and II.

Procedures

Procedures of Polymerization and Liquid Polymer of Polysulfide Polymer

The specified mixture of bis(2-chloroethyl)formal and TCP was reacted at $\sim 80-90^{\circ}$ C with excess of Na₂S_x (x = 1.8-2.3) containing a small quan-



Figure 5 DSC of LP and cured LP.



strain(%)

Figure 6 Stress-strain curve of cured sample D and cured sample F by lead dioxide.

tity of sodium sulfonate (e.g., $1 \text{ cm}^3/\text{mol}^{-1}$ feed monomer) and colloidal magnesium hydroxide. After feeding of monomers, temperature was increased and maintained > 100°C for ~ 1–3 hours (toughening time). After polymerization the residual polysulfide was diluted with water, decanted, and washed away. The purified dispersion was mixed with the reducing salts (sodium sulfite and sodium hydrosulfide) and was kept at 85°C for 1 h under agitation. Some of polysulfide groups were reduced to disulfide and thiol as shown in eqs. (2)– (4). At the end of this procedure, the dispersion was neutralized with acids, washed with hot water to remove salts, and dried to remove water < 0.2 wt % at 90°C under vacuum with water jet pump.

Procedure of Cured LP

Cured LP was prepared by mixing and kneading LP 100 parts and carbon 30 parts by 3 roll mill and handmixing these base compounds with curing pastes made also by 3 roll mill as shown in Table III. These pastes were poured into the metal mold and held between 2-mm sheet and cured at 20°C for 1 day. The dumbbell specimens were cut from the flat sheet by Die C.⁶ These cured LP were subjected to tensile and other measurements.

Measurements

Cl content in LP was measured by X-ray fluorescence analysis on a Rigaku X-ray Analyzer. Amplitude of Cl–K α (4.7276 Å) of sample by X-ray fluorescence was proportional to Cl content in LP. OH content in LP was measured by infrared spectroscopy. SH content of cured LP was measured by a Fourier transform infrared (FTIR) instrument. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer DSC-2C with a temperature increment of 20°C/min under nitrogen. The sample amount was 30 mg. ¹³C-NMR was measured on a JEOL JUM-GX-270 type at 67.8 MHz and the scan was conducted 30,000 times to get signal-to-noise (S/N) ratio sufficient enough to quantify. Solvent was CDCl₃ and all chemical shifts were measured relative to trimethyl silane (TMS).

RESULTS AND DISCUSSION

Time Course of the Polymerization

To elucidate the time course of the polymerization, chlorine contents in LP were determined at hourly intervals during polymerization or toughening time. These results are shown in Figure 1. The more excess of Na_2S_r in the monomer mixture, the faster the decrease in chlorine content. Usually, the content of chlorine in LP was < 100ppm after the polymerization. Even if the content of OH in LP was very low, the cured LP's modulus increased as shown in Figure 3. Generation of OH in LP during polymerization OH content in LP was determined, and it was found to be nearly constant during polymerization or toughening time as shown in Figure 2. This result suggests that the rate of eq. (1) may be very rapid and is inconsistent with the toughening theory, according to whether its content should change during toughening time.

Influence of Toughening Time on Cured LP's Modulus

Figure 3 shows the influence of toughening time on cured LP's modulus where the condition to cure was 1 day at 20°C. Cured LP's modulus increased with the toughening time even if the content of nonreactive end groups in LP, such as Cl or OH, were very low. This phenomenon suggests that some crosslinkings not assigned to TCP have occurred during the polymerization.

Residual SH in Cured LP

Residual SH was not detected by infrared (IR) method in cured LP after mixing LP and lead



Figure 7 ¹³C-NMR spectrum of sample F.

dioxide and reacted for 1 day at 20°C. Figure 4 shows the IR chart of cured sample D by FTIR. There is no absorption peak at 2561 cm⁻¹ of SH. The conversion of SH was estimated to be > 95% from the identification limit of this FTIR technique.

Glass Transition Temperature of LP and Cured LP

Figure 5 shows a DSC chart of sample D and cured sample D. Glass transition temperature is the inflexion point of these curves. Judging from these curves, glass transition temperature of LP is estimated to be -58° C and that of cured LP -52.7° C. These results are in good agreement with the value (-59° C) reported by Bertozzi.³

S-S Curve of Cured LP

Tensile S–S curves of cured samples D and F are shown in Figure 6, where test temperature was 20°C and test strain rate was 500 mm/min. The curing agent was lead dioxide. Tensile S–S behavior of rubbery materials is usually analyzed by

$$\sigma = \nu R T (\alpha - \alpha^{-2}) \tag{5}$$





	Assigned to Trichloropropane		Not Assigned to Trichloropropane		
	(1)	(2)	(3)	(4)	(5)
Chemical shift (ppm)	49.6	50.6	32.8	56.9	92.5
Chemical structure	1	1	2	3	2
Sample A	0.00	0.00	0.24	0.41	0.13
Sample F	0.20	0.12	0.57	0.38	0.08

Table IV Peak Number of Tertiary Carbon of LP Measured by ¹³C-NMR (INEPT)—Chemical Shift and Their Structure and Content on the Basis of $-OCH_2O-$

Notes: 1: ~ SSCH₂CHCH₂SS ~; 2: dead terminals; 3: ~SSCHCH₂O ~ \mid SS ~ SR

According to eq. (5), stress (σ) is proportional to the crosslinking density (ν) at constant strain (α). So stress at 300% elongation ($\alpha = 4$), i.e., 300% modulus, is also proportional to the crosslinking density in the cured LP from eq. (5). As already explained earlier, we discussed and the crosslinking density.

Crosslinking Sites Detected as Tertiary Carbons (CH)

Figure 7 shows the ¹³C-NMR spectrum of sample F (content of TCP is 2 mol %), and Figure 8 shows those of sample A (content of TCP is 0 mol %) and sample F by the INEPT method. The secondary carbons (CH_2) and primary carbons (CH_3) were detected on the negative side, while the tertiary carbons (CH) were detected only on the positive side. Therefore, we could determine which carbons are CH by comparing the spectrum in Figure 7 with that in Figure 8. In Figure 7, peak at 95 ppm is -OCH₂O-, peaks at 65 and 38 ppm are -OCH₂CH₂SS-, peak at 31.5 ppm is -OCH₂CH₂S-, and peak at 24 ppm is —CH₂CH₂SH. Mazurek and Moritz⁵ studied the ¹³C-NMR of polysulfide prepolymer by the distortionless enhancement by polarization transfer (DEPT) method. Peak numbers 1, 2, and 4 of our study in Figure 8 were coincident with those of their study. From Figures 7 and 8, there were two kinds of CH. One group was detected only in sample F and this group (peak No. 1 at chemical shift: 49.6 ppm, peak 2 at chemical shift: 50.6 ppm) was assigned to the CH from TCP. The other group was detected both in samples A and F, and this CH group (peak No. 3 at chemical shift: 32.8 ppm, peak 4 at chemical shift: 56.9 ppm, and peak 5 at chemical shift: 92.5 ppm) was estimated to be produced during polymerization reaction. NMR results of samples A and F on tertiary carbons are shown in Table IV.

We consider that there are three kinds of CH structures that are not assignable to TCP, as shown below:

$$\sim \begin{array}{c} \mathrm{SCH_2CH_2OCHOCH_2CH_2S} \sim \\ | \\ \mathrm{SR} \sim \end{array} \tag{6}$$

$$\sim \text{SCH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2 \sim | (7) \\ \text{SR} \sim (7)$$

$$\sim \begin{array}{c} \text{SCHCH}_2\text{OCHOCH}_2\text{CH}_2\text{SCH}_2 \sim \\ | \\ \text{SR} \sim \end{array} \tag{8}$$

The chemical shift of an α carbon of —CHSR is at a higher magnetic field by 30–40 ppm than that of an α carbon of —CHOR. So we can assume that the chemical shift of the —CHSR of eq. (6) is ~ 72–82 ppm, that of the —CHSR of eq. (7) is ~ 66–86 ppm, and that of the —CHSR of eq. (8) is ~ 48–58 ppm.⁷ The CH structure of peak No. 4 is estimated to be that shown in eq. (8) from the chemical shift.

From these results, possible chemical structures of crosslinking sites are proposed in Table III. Table I shows five kinds of CH, their amounts in different kinds of LP, and the 300% modulus of its cured LP. Numbers 1 and 2 were proportional to the amount of CH peaks in TCP. The amount of peak No. 4 was increased if toughening time of sample A is longer. The amount of peaks 3 and 5 did not depend on either the content of TCP nor on toughening time. Their terminals don't appear to be active like SH, but dead terminals such as alkyl, Cl, OH, or vinyl. So we neglected peaks 3 and 5. Peak No. 4 is a new crosslinking site that is produced in polymerization and has much influence on cured LP's modulus.



Figure 9 Relationship between sum of intensity of peaks No. 1, No. 2, and No. 4 and 300% modulus.

Figure 9 shows the relationship between the 300% modulus of cured LP and the amount of tertiary carbon, i.e., total CH amount of peak Nos. 1, 2, and 4. The correlation of the 300% modulus of cured LP and the sum of these three peaks is good.

According to eq. (5), the modulus, which in this case is the stress at constant elongation, is proportional to crosslinking density ν . Tertiary carbons of peaks 1, 2, and 4 are crosslinking sites. Their amount, i.e., crosslinking density, influences the physical properties of cured LP.

Reaction scheme resulting in the formation of the structure shown in eq. (8) (i.e., peak 4) during polymerization seems to be as follows:

$$\sim \ SSCH_2CH_2OCH_2OCH_2CH_2SS \sim + \ Na_2S_2$$

$$\rightarrow \sim \text{SSCHCH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{SS} \sim + \text{NaSH}$$

|
SNa

$$\begin{array}{ll} \rightarrow & \sim & {\rm SSCHCH_2OCH_2OCH_2CH_2SS} \sim \\ & \mid \\ & {\rm S} \sim {\rm SNa} \end{array}$$

CONCLUSIONS

We studied the polysulfide polymerization to form LP and the mechanical properties of cured LP. As the toughening time was increased, content of unreacted chlorine in LP was decreased, and the cured LP's modulus was increased. According to the toughening theory, OH terminals in LP are removed and decrease during the toughening period.³ But the OH terminals in the polymer of our study did not change or increased little. This inconsistency suggested that additional crosslinking sites concerning tertiary carbon atoms are produced during the polymerization besides TCP.

We have determined the amount of CH in LPs by ¹³C-NMR and the INEPT method. The tertiary carbons in the LPs are not only caused by the TCP units, but also by the few structures that were produced during the polymerization. One of their tertiary carbons afforded crosslinking points and it influenced the physical properties of cured LP. The CH, which is not related to the physical properties, seems to have terminals such as alkyl, Cl, OH, or vinyl.

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NOMENCLATURE

- CH tertiary carbon
- CH₂ secondary carbon
- CH₃ primary carbon
- LP liquid polysulfide polymer
- R gas constant
- T temperature
- TCP trichloropropane
- α strain
- ν cross-linking density
- σ stress

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