

Cationic Cyclization of Neoprene with a Diethylaluminum Chloride and Organic Chloride Catalyst System

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Received 17 April 2001; accepted 13 February 2002

ABSTRACT: The cyclization of neoprene was achieved with the aid of a cationic catalyst system based on diethylaluminum chloride (Et_2AlCl) and an organic chloride, allyl chloride ($\text{CH}_2=\text{CHCH}_2\text{Cl}$) or benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$). The main parameters of the cyclization process were investigated. Elastomers with low intrinsic viscosity, ready solubility and some gelling were obtained. Xylene was a good solvent for the cyclization process, which took place in a very short time (≤ 5 min). The products were characterized

with IR, $^1\text{H-NMR}$, differential scanning calorimetry, and gel permeation chromatography. The polycyclic structure was determined. The degree of cyclization and the incorporated solvent content were estimated with a $^1\text{H-NMR}$ method. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2227–2231, 2002

Key words: rubber; cationic cyclization; elastomers; modification

INTRODUCTION

Cyclized rubbers are used in the formulation of adhesives, inks, and paintings and also in the compounding of natural rubber (NR) to improve its mechanical characteristics. Much work was reported on the cationic cyclization of polyisoprene, NR, and *cis*-1,4-polybutadiene (BR) before the 1980s.¹ However, there still are many patents being issued for which cyclized rubbers are important components in the formulations.²

The structure of cyclized rubbers is still not well understood. Kossler et al.³ investigated the structure of completely cyclized BR by IR spectroscopy and iodometric analysis. They concluded that long sequences (up to 20 units) of orthocondensed cyclohexane rings were formed after long reaction times. However, Priola et al.⁴ used IR and $^{13}\text{C-NMR}$ spectra to study the structure of partly cyclized BR, and they realized that the average length of the polycyclic sequences was between 2.5 and 4, depending on the extent of cyclization.

The cyclization of styrene–butadiene rubber (SBR) with a Lewis acid, AlCl_3 or TiCl_4 , and a cocatalyst (some organic halide system) was reported, but it was not very successful. For example, the intrinsic viscosity ($[\eta]$) of cyclized SBR was higher than that of un-

treated SBR because the Lewis acid was not really suitable for the cyclization.⁵ Cationic catalyst systems based on alkyl aluminum chloride and an organic halide are excellent for the cyclization of BR, so the cyclization of SBR can also be achieved with them.⁶

It is well known that there is a little cyclic structure in neoprene due to cyclization, but the further cationic cyclization of neoprene has been seldom reported until now. We have done some work on the cationic cyclization of diene rubbers with alkyl aluminum chloride and organic halide systems.^{6–9} In this study, we aimed to obtain cyclized neoprene with a low value of $[\eta]$, ready solubility, and some gelling by diethylaluminum chloride (Et_2AlCl) and an organic chloride, allyl chloride ($\text{CH}_2=\text{CHCH}_2\text{Cl}$) or benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$). The cyclized products are expected to be useful as photoresists with high photosensitivity.

EXPERIMENTAL

A commercial neoprene sample (90% *trans*-1,4, 9% *cis*-1,4, and 1% 1,2 and 3,4; molecular weight = 1.3×10^5) was supplied by Jihua Co. (China). It was dissolved in xylene, and the solution was filtered through a G2 sintered glass filter. Et_2AlCl (Carl Roth Co., Germany) was used as received. Allyl chloride was dried with a 4-Å molecular sieve and distilled before use. Benzyl chloride was purified by distillation and showed a boiling point of 177–179°C. Pure-grade solvents such as xylene, methanol, and chloroform were used without further purification.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29574179.

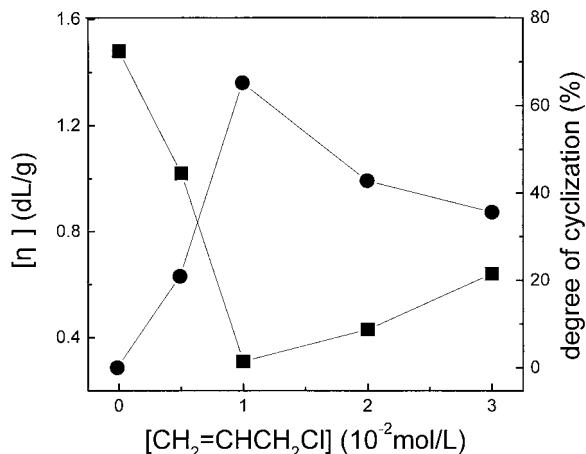


Figure 1 Influence of the $\text{CH}_2=\text{CHCH}_2\text{Cl}$ concentration on neoprene cyclization {[neoprene] = 0.9% (w/v), solvent = xylene, $[\text{Et}_2\text{AlCl}] = 0.01$ mol/L, $t = 20$ min, and $[\eta]$ of untreated neoprene = 1.48 dL/g}: (■) $[\eta]$ and (●) degree of cyclization. The degree of cyclization was calculated from $^1\text{H-NMR}$ spectra.

Cyclization reactions were carried out in a two-necked, flat-bottom flask equipped with a magnetic stirrer, a thermometer, and a dropping funnel condenser and were maintained under a dry N_2 atmosphere. The necessary amount of allyl chloride or benzyl chloride was added to the polymer solution, and the mixture was heated to 40 or 120°C, respectively. The solution of Et_2AlCl was slowly dropped into the polymer solution, which was allowed to react for 20 min. The cyclization process was terminated with ethanol. The reaction mixture was washed with distilled water three times. The polymer was coagulated in an excess of ethanol and dried in vacuo at 40°C for 24 h. The degree of cyclization was obtained by the $^1\text{H-NMR}$ method.

$[\eta]$ data were obtained by relation viscosity measurements with the relationship proposed by Solomon and Ciută.¹⁰ IR spectroscopic measurements were made with a Bio-Rad FTS-7 spectrometer for polymer films cast from CHCl_3 on sodium chloride plates. $^1\text{H-NMR}$ spectra were recorded with a Varian Unity 400-MHz NMR spectrometer from polymer solutions (in CDCl_3) at 25°C (tetramethylsilane was the internal

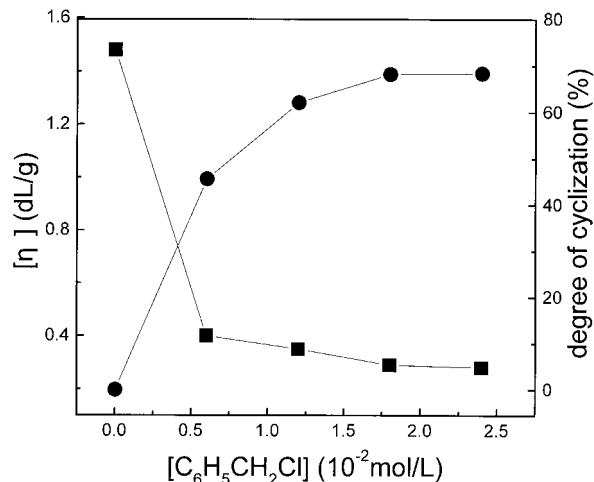


Figure 2 Influence of the $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ concentration on neoprene cyclization {[neoprene] = 1.5% (w/v) and $[\text{Et}_2\text{AlCl}] = 0.012$ mol/L; for the other conditions, see Fig. 1}: (■) $[\eta]$ and (●) degree of cyclization.

standard). Differential scanning calorimetry investigations were performed with a PerkinElmer instrument, usually at a heating rate of 10°C/min. Gel permeation chromatography (GPC) measurements were carried out with a Waters 410 instrument in a tetrahydrofuran polymer solution at 25°C.

RESULTS AND DISCUSSION

Cyclization of neoprene

When Et_2AlCl is slowly dropped into a polymer solution, it drastically reacts with allyl chloride or benzyl chloride, and cationic active species are formed. They attack and open the double bond of neoprene, which is cyclized. Many cyclic structures are formed in the linear macromolecule chain. Therefore, high levels of cyclization are always accompanied by a sharp reduction in the $[\eta]$ value. In the cyclization process, a neoprene xylene solution is pearl yellow at first, becomes black when Et_2AlCl and an organic chloride are added, and then becomes clear again after the terminator ethanol is added. Et_2AlCl can react with an organic chloride and yield cationic active species,

TABLE I
Solubility of the Cyclized Neoprene

	Solvent					
	Chloroform	Dichloroethane	Xylene	Toluene	Benzene	Cyclohexane
N-1 (%) ^a	90.2	90.1	80.3	85.6	81.2	77.8
N-2 (%) ^a	90.3	90.1	82.4	89.2	84.5	80.3
C-1 (%) ^b	70.4	66.6	42.4	57.5	45.7	6.6
C-2 (%) ^b	82.5	78.5	53.2	70.0	56.1	10.2

^a By the $\text{Et}_2\text{AlCl}/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ system and for 4 h.

^b By the $\text{Et}_2\text{AlCl}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ system and for 24 h.

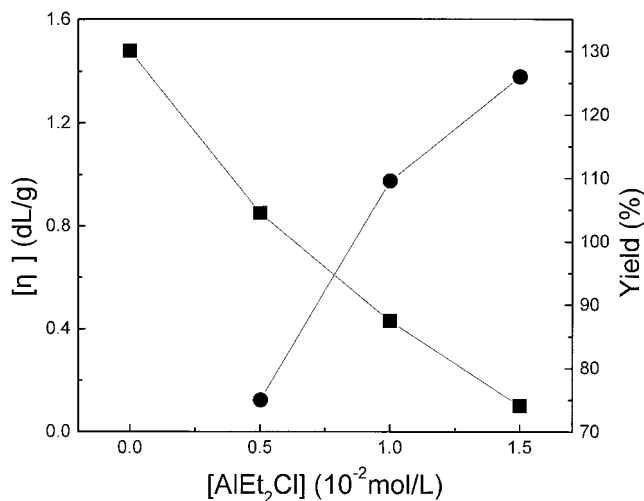


Figure 3 Influence of the Et_2AlCl concentration on neoprene cyclization ($[\text{CH}_2=\text{CHCH}_2\text{Cl}] = 0.02 \text{ mol/L}$; for the other conditions, see Fig. 1): (■) $[\eta]$ and (●) yield.

which can form a stable complex with the solvent xylene. The complex makes the mixture solution fuscous. In the same time, a large amount of heat energy dissipates during the cyclization process because of the reaction between Et_2AlCl and the organic chloride and the opening of the double bond of the neoprene macromolecular chains.

Figure 1 shows the influence of the allyl chloride concentration on neoprene cyclization. Allyl chloride is a low-boiling-point compound and is used as a cocatalyst at a low reaction temperature (40°C) and a low polymer concentration (0.9% w/v). In fact, in the presence of allyl chloride, an efficient cyclization takes place that increases in extent with an increase in the allyl chloride concentration at first. When the $\text{CH}_2=\text{CHCH}_2\text{Cl}$ concentration is 0.01 mol/L, $[\eta]$ decreases to a minimum value, and the degree of cyclization increases to a maximum value. With a further increase in the allyl chloride concentration, $[\eta]$ increases, and the degree of cyclization decreases gradually. This means that excess allyl chloride is not favorable for the cyclization of neoprene at a low reaction temperature. Cyclized products from the $\text{Et}_2\text{AlCl}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ system are elastomeric, and the color changes from yellow to brown to black with an increase in the degree of cyclization. In this work,

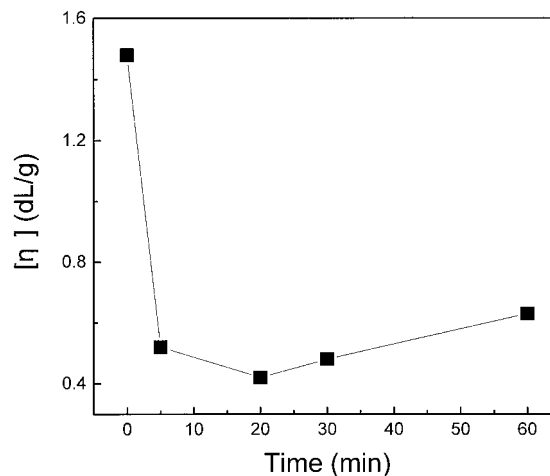


Figure 4 Influence of the reaction time on neoprene cyclization ($[\text{CH}_2=\text{CHCH}_2\text{Cl}] = 0.02 \text{ mol/L}$ and $[\text{Et}_2\text{AlCl}] = 0.01 \text{ mol/L}$; for the other conditions, see Fig. 1).

the yield of cyclized neoprene under most reaction conditions is greater than 90% and sometimes greater than 100%, especially with the $\text{Et}_2\text{AlCl}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ system.

Benzyl chloride has the good cocatalytic activity, high stability, and low volatility needed for a high reaction temperature. Figure 2 shows the influence of the benzyl chloride concentration on neoprene cyclization. The cyclization process is carried out at a 1.5% (w/v) polymer concentration at a high reaction temperature (120°C). A sharp reduction in $[\eta]$ and a sharp increase in the degree of cyclization take place at a very low benzyl chloride concentration. At a higher benzyl chloride concentration, $[\eta]$ decreases, and the degree of cyclization increases continuously. A possible reason for this is that, at a high reaction temperature, the degradation process becomes more important. The cyclized products from the $\text{Et}_2\text{AlCl}/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ system are plastic brown.

We investigated the solubility of cyclized products. Cyclized neoprene (0.01 g) was dissolved in 20 mL of different solvents without stirring for a certain time, and then the solutions were filtered through a G2 sintered glass filter. The cyclized neoprene that was not dissolved was dried in vacuo at 40°C for 24 h and weighed; the solubility was then obtained. The results are listed in Table I. The solubility of the cyclized

TABLE II
Influence of Neoprene Concentration on the Cyclization Reaction

[Neoprene] (% w/v)	$[\text{Et}_2\text{AlCl}]$ (mol/L)	$[\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]$ (mol/L)	$[\eta]$ (dL/g)	Gel content (%)	Yield (%)
1.5	0.012	0.012	0.35	4.4	91
3	0.02	0.02	0.28	17.2	95
6	0.02	0.02	—	Large amount	120

Conditions: $T = 120^\circ\text{C}$, $t = 20 \text{ min}$, solvent = xylene.

TABLE III
Influence of Solvent on the Cyclization of Neoprene

Solvent	$[\eta]$ (dL/g)	Gel content (%)	Yield (%)
Benzene	0.19	56	115
Toluene	0.20	45	113
Xylene	0.50	Little	109

Conditions: [neoprene] = 1%, $[\text{Et}_2\text{AlCl}] = 0.01$ mol/L, $[\text{CH}_2=\text{CHCH}_2\text{Cl}] = 0.02$ mol/L, $T = 40^\circ\text{C}$, $t = 20$ min.

neoprene from the $\text{Et}_2\text{AlCl}/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ system is better than that of the cyclized neoprene from the $\text{Et}_2\text{AlCl}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ system. The solubility in chloroform is best, and that in cyclohexane is worst.

Figure 3 shows the influence of the Et_2AlCl concentration on neoprene cyclization. With an increase in the Et_2AlCl concentration, $[\eta]$ of the cyclized neoprene decreases gradually. This means that the cyclization of neoprene is enhanced, and the degree of cyclization is increased. In the same time, the yield of cyclized products increases with an increase in the Et_2AlCl concentration. Surprisingly, at a high Et_2AlCl concentration, the yield is far greater than 100%. We think this occurs because the solvent xylene is incorporated into the polymer chain during the cyclization process; this is discussed later.

Figure 4 shows the influence of the reaction time on the cyclization of neoprene. The largest part of the cyclization occurs within 5 min (or less), and the $[\eta]$ value is smallest in 20 min. With the longer reaction time, the crosslinking process is more serious, and $[\eta]$ increases. Therefore, the cyclization reaction time is commonly fixed at 20 min.

The neoprene concentration needed for the cyclization process is very low at 40°C with the $\text{Et}_2\text{AlCl}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ system. However, it is possible that the polymer concentration is increased at 120°C by the use of the $\text{Et}_2\text{AlCl}/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ system. In Table II, the results obtained with different concentrations of neoprene are reported. When the polymer concentration increases, intramolecular crosslinking reactions become favored, and as expected, a gel appears.

Table III collects the results obtained from different solvents, displaying different basicity values, at 40°C . The $[\eta]$ value of the cyclized product obtained in benzene and toluene is small, but the gel content is very high, so they are fine for the cyclization reaction. In xylene, neoprene can be cyclized readily, and the gel content is very small, so xylene is a fine solvent for the cyclization process. Xylene probably forms a stable Friedel-Crafts complex with the cationic species more easily. The same results have been obtained for the cyclization of polybutadiene¹¹ and SBR.⁶

Characterization of cyclized neoprene

The IR spectra of cyclized neoprene from the $\text{Et}_2\text{AlCl}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ and $\text{Et}_2\text{AlCl}/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ systems

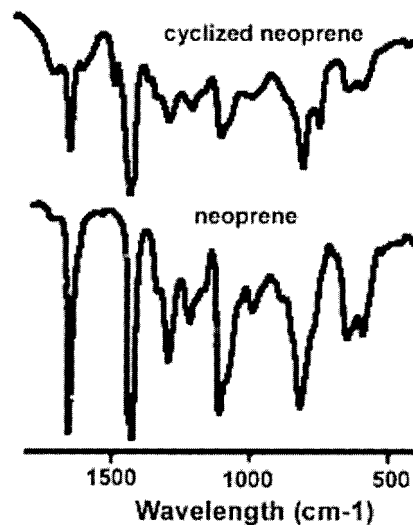


Figure 5 IR spectra of neoprene and its cyclized product.

are similar. The IR spectra of neoprene and cyclized neoprene are similar from 4000 to 2000 cm^{-1} and different from 2000 to 400 cm^{-1} . In Figure 5, we can see that the IR spectrum of neoprene has a 1658-cm^{-1} peak (double bond, $\text{C}=\text{C}$) and a 824-cm^{-1} peak (anti-1,4-unit, $=\text{CH}$). In the IR spectrum of the cyclized products, the intensity of the peaks relative to the double bond weakens and fades away. Two new peaks at 759 and 818 cm^{-1} are given by the benzene ring of xylene, which is incorporated into the polymer chain in the cyclization process.

In the $^1\text{H-NMR}$ spectrum of cyclized neoprene, the intensity of the peaks at 5.45 and 5.20 ppm, which are signals of the double bond, weakens (see Fig. 6). Peaks from 1.0 to 3.0 ppm are broadened and enhanced, and they can be assigned to nonequivalent methylene groups present in cyclic saturated structures. The peak at 7.0 ppm is the signal of the benzene ring because the

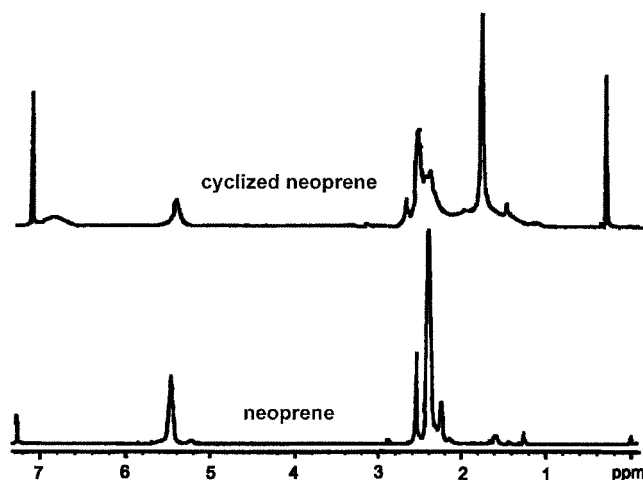


Figure 6 $^1\text{H-NMR}$ spectra of neoprene and its cyclized product.

TABLE IV
 T_g and T_m of Neoprene and Cyclized Neoprene

	$[\eta]$ (dL/g)	T_g (°C)	T_m (°C)
Neoprene	1.48	-41.6	50.5
Cyclized neoprene-1	0.85	-37.7	50.5
Cyclized neoprene-2	0.43	-27.9	99.2
Cyclized neoprene-3	0.10	-14.0	127.1

solvent xylene is incorporated into the polymer chain. One can calculate the degree of cyclization of cyclized neoprene and the incorporated solvent xylene content in polymer chains from $^1\text{H-NMR}$ spectra.

Table IV shows that the glass-transition temperature (T_g) and melting point (T_m) of cyclized neoprene rise with an increase in the degree of cyclization. During the cyclization process, a double bond of the macromolecular chain is opened, and a cyclic structure is formed. The rigidity of the polymer chain increases, so T_g and T_m increase, and the polymer loses its elasticity and becomes a plastic or powder.

The differential molecular weight distribution curves obtained by GPC analysis for neoprene and cyclized neoprene are plotted in Figure 7. Both distributions are monomodal, and the curves are symmetric. The peak of the diagram of the cyclized polymer is broader than that of neoprene. Even though the interpretation of these diagrams is complicated by the modification of the polymer structure, they seem to indicate that some chain breaking and branching reactions occur during the cyclization treatment.

Cyclization mechanism

As shown in the literature, the cyclization process is usually carried out in an extremely dilute solution, and the intramolecular reaction for macromolecules is

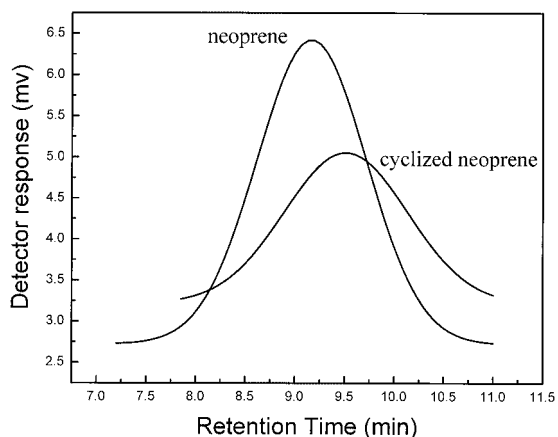
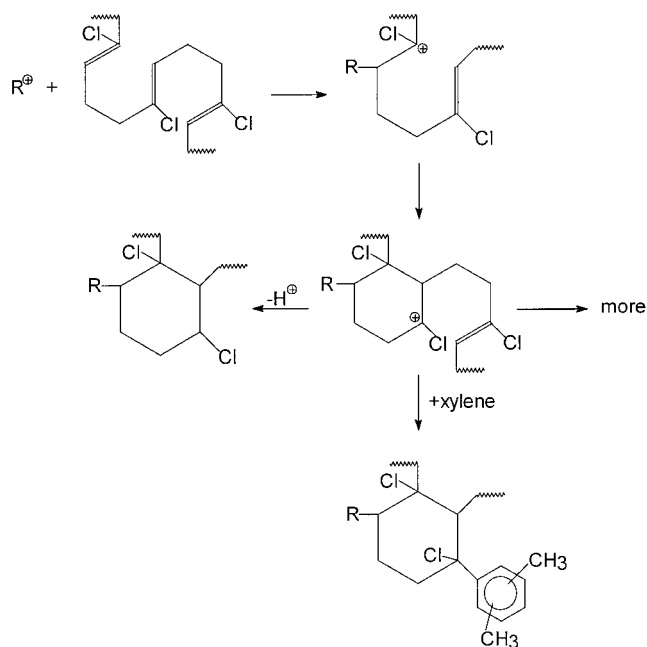


Figure 7 GPC of neoprene and its cyclized product.



Scheme 1

more favorable; that is, cyclization is neither a scission of the polymer nor an intermolecular reaction.¹² The solvent xylene is incorporated into the polymer chain in the cyclization process because of the chain-transfer reaction. In this study, we used a Lewis acid catalyst (Et_2AlCl) and a cocatalyst (an organic chloride, $\text{CH}_2=\text{CHCH}_2\text{Cl}$ or $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$) to cyclize neoprene. The cyclization of neoprene can proceed as shown in Scheme 1.

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