

Low-Temperature Cross-linking of Polychloroprene Rubber with "DYTEK" A Amine

INTRODUCTION

Polychloroprene rubber (CR) is the first commercial synthetic elastomer. The chlorinated olefin backbone of polychloroprene is less reactive than is the backbone of natural rubber and polybutadiene, and its vulcanizates possess excellent oil resistance, good solvent resistance, and chemical resistance. These properties combined with its good strength and nonflammability have kept polychloroprene in a very important place among the special purpose elastomers.

The traditional cross-linking of polychloroprene is based on the highly reactive tertiary allylic chlorine atoms of the 1,2 units present in small amounts ($\sim 1.5\%$) along the polymer chain. The preferred cross-linking agents are zinc oxide and magnesium oxide, which serve to abstract the chlorine¹ (see Scheme 1).

It was proposed by Kovacic² that bifunctional diamines can be used to cross-link polychloroprene through a bis-alkylation reaction involving chlorine removal in the presence of certain metal oxide such as magnesium oxide (Scheme 2).

The bisalkylation theory of cross-linking of CR by bifunctional diamines was confirmed by Hepburn and Mahdi³ using amine-bridged amides as cross-linking agents. But the curing temperatures for cross-linking of CR in the above processes are usually high (around 150°C). It is known that polychloroprene (CR), like poly(vinyl chloride) (PVC), is a polymer that is particularly sensitive to effects of heat and mechanical stressing.^{4,5} These effects induce some undesirable reactions in the polymer, such as oxidation of the polymer chain, dehydrochlorination, and chain scission combined with the production of reactive macroradicals, leading eventually to degradation cross-linking. Because of the thermal degradation behavior of CR, it is of practical interest to cross-link CR at low temperature. In this article, we report on the cross-linking reaction of CR with bifunctional "DYTEK" A amine (2-methylpentamethylenediamine) at low temperature of 60°C and the subsequent characterization of the cross-linked CR elastomer.

EXPERIMENTAL

Materials

The original white elastic polychloroprene (10% *cis*, 85% *trans*, $M_w = 2.9 \times 10^5$; $\rho = 1.23 \text{ g/cm}^3$; $T_g, -48^\circ\text{C}$; $T_m, 115^\circ\text{C}$) was provided by Aldrich Chemical Co. No color

change was observed in the polymer under storage in the dark. "DYTEK" A amine (98.5%) was a gift from Dupont Co. It is a colorless liquid with a weak ammonia odor. ACS-certified potassium iodide KI (Fisher Scientific), which was used in the experiment, is a white crystalline solid. The above chemicals were used as received without further purification. All solvents used were of reagent grade and dried over Linde 4Å molecular sieves.

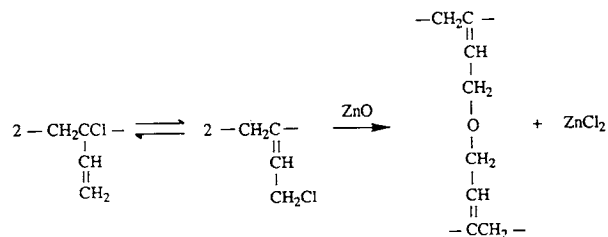
Potassium Iodide-treated Polychloroprene

Potassium iodide (KI) was dissolved in benzene and dimethyl sulfoxide (DMSO) mixed solvent ($V_{\text{benz}}/V_{\text{DMSO}} = 87 : 13$) with a KI concentration of $1.09 \times 10^{-5} \text{ mol cm}^{-3}$. The solution was homogeneous and colorless. Linear CR was dissolved in this KI solution at room temperature under a N_2 atmosphere to a concentration of 1.0 g polymer per 15 mL solution. The dissolved polymer solution was slightly milky. The solution was heated in a closed bottle for 7 h at 60°C . We believe that during the heating process the 1,2 units in polychloroprene are iodinated following Scheme 3.

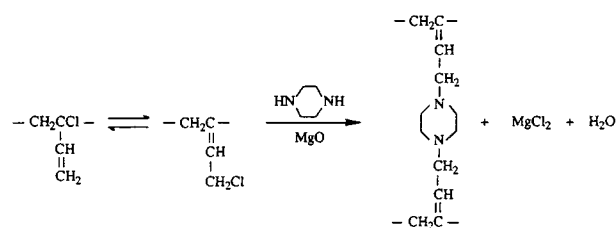
In the experiment, a white precipitate was observed during the heating process. The solution became colorless and transparent after standing in the hood. The KI-treated polychloroprene solution was kept in a refrigerator for subsequent use.

Cross-linking of Polychloroprene with "DYTEK" A Amine

To the clear KI-treated CR solution, $8.45 \times 10^{-5} \text{ mol di-amine per gram polymer}$ was added with stirring at room temperature for 1 h under a N_2 atmosphere. The solution was allowed to stand at room temperature overnight and it turned slightly yellow in color. The solution was poured into an aluminum dish that was placed in the oven at 60°C for 48 h under a N_2 atmosphere. The film was then further dried another 24 h at 60°C under vacuum. The



Scheme 1



final product was a soft, translucent elastomer, deep brown in color. The cured CR network did not dissolve in either chloroform or benzene (both good solvents for linear CR); however, swelling of the sample did occur to about twice its initial dimensions. In contrast, the linear CR film that was cast under the same conditions as cross-linked CR totally dissolved in chloroform, benzene, and toluene at room temperature. The extractable components in cross-linked CR were only 5 wt % after 24 h Soxhlet extraction with chloroform. The average molecular weight between two cross-links, \bar{M}_c , was 10.2×10^3 , as determined from a swelling experiment⁶ performed in benzene.

PHYSICAL MEASUREMENTS

Calorimetric Measurements

The glass transitions (T_g 's) were measured by differential scanning calorimetry (DSC, DuPont 2000). Measurements were carried out from -80 to $+80^\circ\text{C}$ under nitrogen at a scanning rate of $20^\circ\text{C}/\text{min}$. Specimen sizes were of the order of 15 mg.

Electron Microscopy

The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM). The specimens for SEM were frozen in liquid nitrogen, fractured, mounted on a stub with silver paint, and coated with gold in a Blazers SCD-004 sputter coater. They were then observed with a digital scanning microscope (DSM 940, Zeiss, Germany) operating at middle voltage. The electron images were recorded directly from the cathode ray tube on Polaroid 55 film.

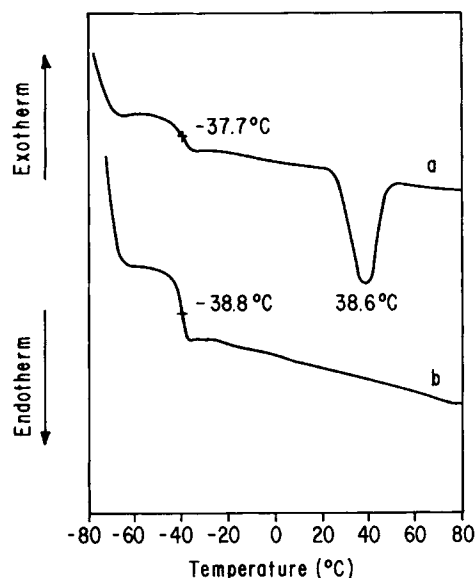
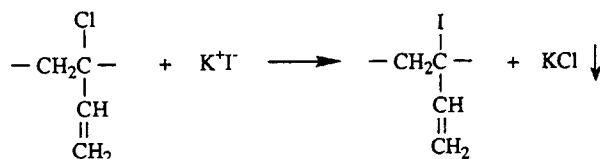
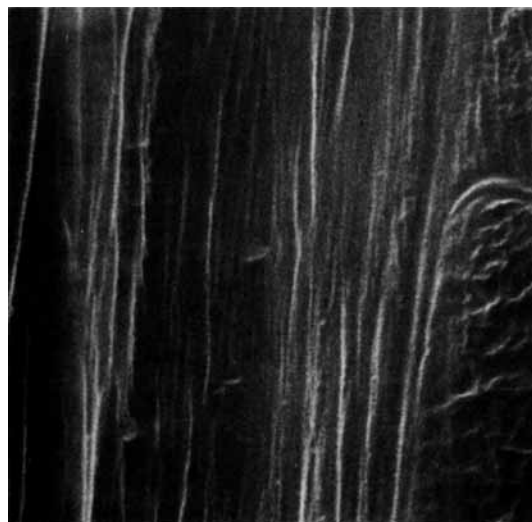


Figure 1 DSC thermograms of CR: (a) linear CR film; (b) cross-linked CR film.

RESULTS AND DISCUSSION

The displacement reaction of the halogen in an alkyl halide by another group, e.g., I^- , is one of the most important reactions in organic chemistry. The replacement of the chlorine atom in the 1,2 unit of CR by I^- (Scheme 3) can proceed virtually to completion because potassium iodide is soluble in the mixed solvents being used and potassium chloride is not. The solubilities of the above inorganic salts in the mixed solvents were also confirmed by using pure KI and KCl, respectively. It makes the above displacement reaction of practical interest because the alkyl iodide has a much lower bond dissociation energy than that of alkyl chloride.⁷ In the experiment, it was important to use a mixed solvent to make both KI and CR polymer soluble, because, in general, a good solvent for KI is a nonsolvent for CR and vice versa. The exceptionally low reactivity of vinyl halides excludes the possibility of replacement of the chlorine atom attached directly on the double bond by I^- under the experimental conditions employed. "DYTEK" A amine was chosen as the cross-linking agent because the 2-methyl branch effectively imparts lower viscosity, greater flexibility, and improved compatibility in a wide variety of formulations.

FTIR spectra were obtained using a Perkin-Elmer Model 1600 spectrophotometer. The IR spectrum of the original material of CR was identical with the one cited in Ref. 8. The results of the IR spectra of linear CR, KI-treated CR, and cross-linked CR were in accord with the expected structures. DSC thermograms obtained from the cast film of linear CR and cross-linked CR are shown in Figure 1. The linear CR exhibited a T_g of -37.7°C and a clear melting point peak at 38.6°C , which shows the crystalline character of the material (curve a). The cross-



(a)

1 μm



(b)

1 μm

Figure 2 SEM of CR: (a) linear CR film, bar = 1 μm; (b) cross-linked CR film, bar = 1 μm.

linked CR exhibited a smooth curve with the best adjusted fit for the T_g transition at -38.8°C (curve b). No endothermic peak was observed here. The slightly lower T_g value of cross-linked CR than that of linear CR could be caused by the greater flexibility of the cross-linking agent, "DYTEK" A amine. SEM micrographs for the linear CR and cross-linked CR are shown in Figure 2. SEM studies

exhibiting the fractured surface of the linear CR film and cross-linked CR confirm the results obtained by the DSC measurements shown in Figure 1. Linear CR with crystallization revealed an aligned dense morphology [Fig. 2(a)] and cross-linked CR exhibited a uniform loose morphology [Fig. 2(b)].

Compared with the cross-linked CR previously prepared by two of us via a free-radical reaction under mild temperature conditions,⁹ the gel content of the present cross-linked CR (95%) was much higher and it was also found to be environmentally much more stable. We expect that this cross-linking technique of CR is interesting for CR vulcanization as well as for CR-IPN synthesis.

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