Use of Trifluoromethanesulfonic Acid As Catalyst for the Cyclization of Polyisoprene

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ABSTRACT: In this study, trifluoromethanesulfonic acid was employed as catalyst for the cyclization of polyisoprene. From ^{1}H nuclear magnetic resonance spectroscopy and gel permeation chromatography investigations, cyclization was confirmed, and the molecular structure variation of polyisoprene during cyclization reaction was determined. With the comparison to that catalyzed by other strong acids (methanesulfonic acid), polyisoprene was cyclized with much higher efficiency, using trifluoromethanesulfonic acid as catalyst. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3666–3669, 2006

Key words: trifluoromethanesulfonic acid; cyclization; polyisoprene; methanesulfonic acid

INTRODUCTION

Polyisoprene rubbers are widely used in the manufacture of tires, mechanical goods, sporting goods, shoes, and sealants. It is the main component of natural rubber, and, in the present day, is synthesized by solution polymerization, using Ziegler–Natta catalysts, in a polymeric industrial plant. Cyclized rubbers are commercially important, with various applications as adhesives, coatings (lacquers and paints), resists, light sensitive compositions, and inks.[1,2] For the purpose of increasing its chemical resistance, cyclization reaction is the most convenient method to achieve this goal.

As it was indicated in the previous researches, natural rubber, treated with strong acids (e.g., sulfuric acid), organic acids (e.g., *para*-toluenesulfonic acid or methanesulfonic acid (MSA)), or Lewis acids (e.g., $SnCl_4$, BF_3, $TiCl_4$, or $FeCl_3$), undergoes progressive resinification so-called cyclization.[3–5] The acid-catalyzed cyclization reaction is a cationic reaction. The available proton adds to a double bond, according to Markownikoff's rule, to form a carbenium ion, and subsequently, the carbenium ion attacks the adjacent olefinic carbons, which leads to a cyclic molecular structure after deprotonation, as illustrated in Scheme 1.[5]

Harita et al. illustrated that fluorine-contained substituted sulfonic acid compounds can be applied as catalyst for the cyclization of conjugated diene polymers.[6] These sulfonic acids are represented by the formula:

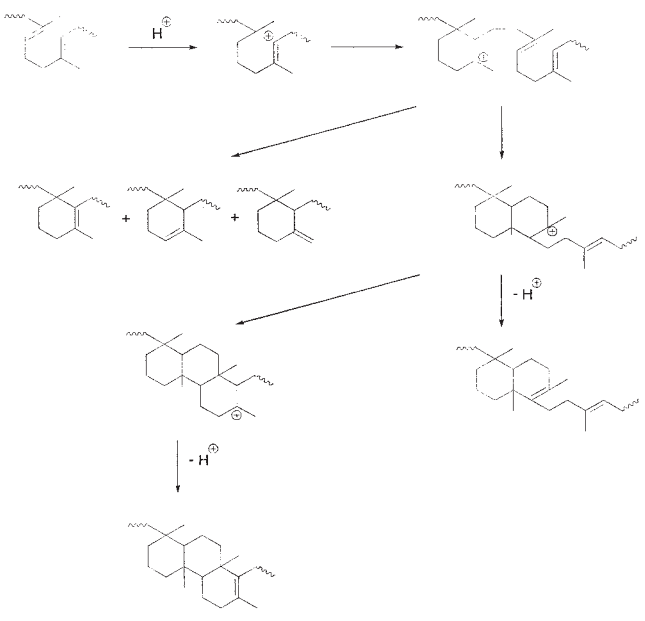
$$CF_nH_{3-n}SO_3R \text{ or } CF_nH_{3-n}SO_2X$$

wherein R is hydrogen or alkyl, X is halogen, and n is 1, 2, or 3. These fluoro-containing substituted sulfonic acids exhibit excellent catalysis efficiency, where smaller amount of catalyst and less reaction time are needed than traditional catalysts applied, i.e., MSA or tin tetrachloride, for the cyclization of conjugated diene polymers.

EXPERIMENTAL

Materials

Polyisoprene rubber, with trade name of IR-307, was purchased from Kraton. Catalysts, trifluoromethane-



Scheme 1 Cyclic molecular structure after deprotonization.

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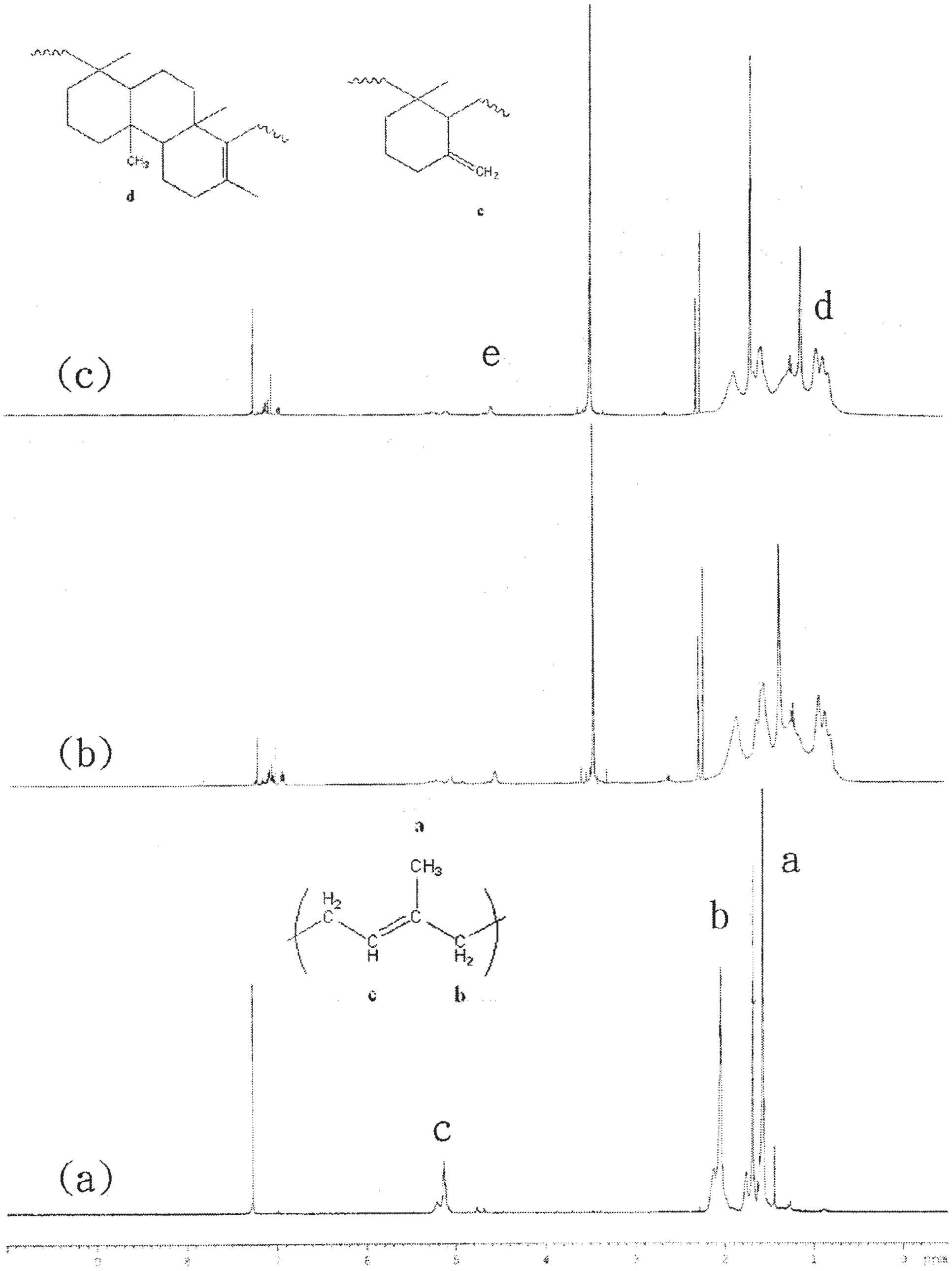

Figure 1 ^{1}H NMR spectra of polyisoprene.

sulfonic acid (TFA) and MSA, were obtained from Merck and Central Glass Co. Ltd., respectively. The solvents: xylene (ACS grade, Tedia) and methanol (HPLC grade, Tedia) were used as received, without further purification.

Cyclization of polyisoprene

To a 500-mL four-necked reactor, 5 g of polyisoprene and 180 g of xylene were added. After the temperature was raised to 75°C, a desired amount of catalyst dissolved in 20 g xylene was fed in 5 min, to perform the reaction under nitrogen atmosphere with rigorous mixing. At specified sampling times, ~3 g of polymer solution was taken and precipitated in methanol. After filtration, the samples were dried in vacuum and stored with seal, for further investigation for 3 days.

Characterization of the synthesized polymers

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a 500 MHz instrument (Varian unity INOVA 500NMR spectrometer), using $CDCl_3$ as a solvent and tetramethylsilane as an internal stan-

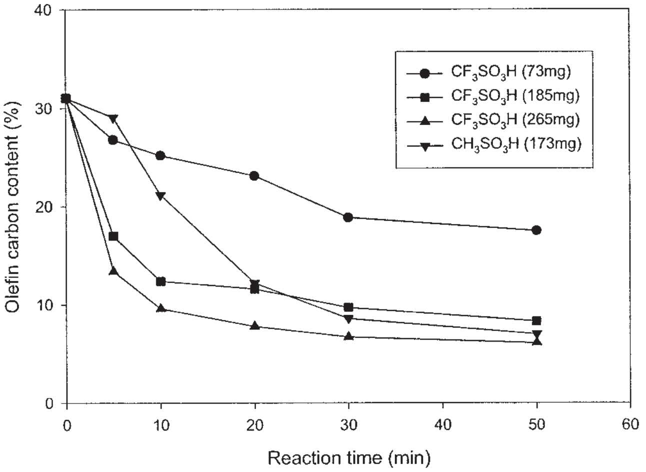

Figure 2 Content of unsaturated carbon in cyclized products.

dard, for examining the olefin carbon content of cyclized polymers. The molecular weight and distribution of the cyclized polyisoprene was determined by gel permeation chromatography (GPC), which was constructed with isocratic HPLC pump (Waters 1515) and refractive index detector (Waters 2410), using tetrahydrofuran as the eluent (flow rate of 1.0 mL/min was used) and polystyrene as the standard.

RESULTS AND DISCUSSION

Molecular structure of cyclized product

Figure 1 demonstrated the ^1H NMR spectra of polyisoprene and its cyclized products for a reaction time of 10 and 30 min, using 189 mg TFA as the catalyst. Distinct chemical shifts that belong to the raw material, polyisoprene, were observed at 1.60, 2.02, and 5.10 ppm. With TFA catalyst for 10 min, the designated chemical shifts, located at 0.95 and 4.55 ppm in NMR spectra, were associated to the cyclized products. These chemical shifts did not develop apparently with further reaction of 30 min. It indicates that cyclization of polyisoprene was confidently accomplished in a short period of 10 min, with 185 mg of TFA catalyst. In addition, there existed complex mechanisms of cyclization of polyisoprene, in which not only one product was generated, as illustrated in Scheme 1.[5]

Unsaturated carbon content

In ^1H NMR spectra, chemical shifts of designated hydrogen atoms on methane, methylene, or methine groups, were well resolved at <1.8, 1.8–4.0, and >4.0 ppm, respectively. Furthermore, the chemical shifts at 4.5–5.5 ppm were related to the hydrogen atoms on olefinic carbons. The content of unsaturated carbon in these cyclized products can thus be calculated, according to the ratio of the integral values for designated chemical shifts. These results were sketched in Figure 2.

In this figure, the olefin carbon content decreased with reaction time, which indicates that the polyisoprene was confidently cyclized via two types and various amounts of sulfonic acid catalyzed. Olefin carbon content of polyisoprene was 31.0%. With 265 mg of TFA catalyst, olefin carbon content of the cyclized product decreased and exhibited lower than that of 73 mg TFA used during cyclization reaction. This indicates that large amount of TFA used can firmly increase the cyclization efficiency of polyisoprene.

On the other hand, olefin carbon content of the cyclized product decreased to ~18.0%, with MSA catalyst. This value exhibits much greater efficiency than that catalyzed by TFA (6.0–8.5%), which indicates the low efficiency of cyclization reaction catalyzed by MSA. In addition, the amount of TFA used for the cyclization of polyisoprene was much less than stannic chloride,[6] which also indicates the high efficiency of cyclization.

Variation of molecular weight during cyclization

It is well known that GPC can be applied for the determination of the molecular weight distribution of polymers or oligomers, by differentiating their retention time passing the column. As shown in Scheme 1, the molecular structure is varied during cyclization of conjugated diene polymers; however, molecular weight is not changed. It induces the retention time of cyclized polymer, and hence, the structure variation of polymer can be traced from GPC profile.

From GPC investigation, molecular weight variation of cyclized polyisoprene during cyclization via TFA and MSA catalyst was sketched in Figure 3. All the molecular weight of cyclized polyisoprene catalyzed via different catalysts and various amount of

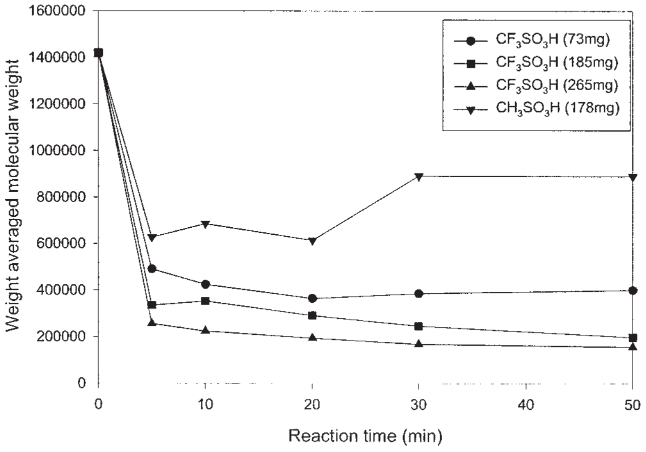

Figure 3 Molecular weight variation of cyclized polyisoprene during cyclization via TFA and MSA catalyst.

catalyst exhibit sudden drop in 5 min of cyclization. In addition, lower molecular weight was obtained by high amount of TFA catalyst, which illustrates the high efficiency of cyclization reactions.

However, it is interesting to notice that with MSA or 73 mg of TFA catalyst, molecular weight of cyclized polyisoprene raised after cyclizing for 30 min. For MSA and 73 mg of TFA-catalyzed cases, molecular weight of cyclized polyisoprene was increased from 615,000 to 892,000 g/mol and 366,000 to 387,000 g/mol, respectively. This phenomenon was not observed for cyclized polyisoprene, catalyzed by a large amount of TFA. According to the study of olefin carbon content in the previous section, olefin carbon content of cyclized polyisoprene decreased continuously with cyclization time, in the all cases in this study. It indicates that a gelation occurred, which resulted in the high molecular weight product after 30 min of cyclization.

CONCLUSIONS

In this study, TFA was employed as catalyst for the cyclization of polyisoprene. From ^{1}H NMR and GPC investigations, polyisoprene cyclized with high efficiency by TFA catalysis was confirmed, which resulted in lower olefin carbon content and lower molecular weight of the cyclized products than those catalysts used traditionally (MSA or stannic chloride). With high amount of TFA catalyst, gelation effect can also be avoided, and the molecular weight was not increased, as MSA or low amount of TFA was used.

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