

수산기 말단 폴리부타디엔을 개시제로 사용한 에피클로로히드린의 양이온 개환 중합과 그 결과물의 아지드화 반응

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Cationic Ring-opening Polymerization of Epichlorohydrin Using Hydroxyl-terminated Polybutadiene as an Initiator Followed by the Azidation of the Resulting Block Copolymer

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초록: 수산기로 말단 변성된 폴리부타디엔을 개시제로 사용하여 에피클로로히드린을 양이온 개환 반응에 의하여 중합시켰다. 촉매는 루이스 산을 사용하였으며, 단량체인 에피클로로히드린을 천천히 반응물에 투입하여, 활성 사슬 말단 메커니즘보다는 활성 단량체 메커니즘에 의하여 중합이 이뤄지도록 하였다. 반응 후, 분별 침전방법에 의하여 생성물에서 삼중블록 공중합체인, 폴리에피클로로히드린-폴리부타디엔-폴리에피클로로히드린을 분리하였다. 하지만, 위 삼중블록 공중합체의 고온에서의 아지드화 반응 시, 반응 완료되기 전, 부분적으로 아지드화된 삼중블록 공중합체와 아지드화가 안된 삼중블록 공중합체들간 반응에 의하여 고분자 사슬들이 엉켜 생성물 내에서 젤화 현상이 일어나, 최종적으로 아지드화 반응을 종결시킬 수 없었다.

Abstract: Epichlorohydrin (ECH) was polymerized through a cationic ring-opening polymerization reaction using hydroxyl-terminated polybutadiene as an initiator. ECH was very slowly added to the reactant mixture containing a Lewis acid catalyst to promote an activated monomer mechanism (AMM) rather than an active chain-end mechanism (ACM). The triblock copolymer PECH-PB-PECH was separated from the resulting polymers using a fractional precipitation method; however, unlike previous reports of the preparation of a fully azidated PECH-PB-PECH, the substitution of the chlorine moiety in PECH with an azide moiety at high temperatures was not completely accomplished due to the entanglement of the partly azidated PECH-PB-PECH and unreacted PECH-PB-PECH.

Keywords: cationic ring opening polymerization, hydroxyl-terminated polybutadiene, azidation, azide-alkene reaction.

Introduction

Glycidyl azide polymer (GAP), prepared via the cationic polymerization of epichlorohydrin followed by the azidation of the resulting polymer, has generated significant interest for its positive effects on the flame temperature and burn rate of nitrate ester plasticized solid propellants due to the presence of the highly exothermic azide ($-N_3$) pendent group in the poly-

mer chain.¹ GAP is also useful as a solid fuel for air-breathing propulsion systems because its monopropellants provide excellent combustion properties.²

In addition to a propellant's performance and vulnerability to hazard stimuli during manufacturing, the environmental impact of a propellant's combustion byproducts must be considered. Ammonium perchlorate (AP) has been widely used as an oxidizer for the production of solid propellants; however, AP releases toxic chlorine products during combustion. Ammonium nitrate may be used in place of AP; however, the resulting propellants frequently display undesirable performance properties. The unique thermal properties of GAP cir-

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cumvent the performance reductions typically observed in propellants that are manufactured using ammonium nitrate instead of AP while avoiding toxic combustion products, thereby rendering GAP an eco-friendly chlorine-free and smokeless propellant.³ Despite its excellent thermal properties, GAP-based solid propellants do not display good mechanical or low-temperature properties compared to conventional hydroxyl-terminated polybutadiene (HTPB)-based solid propellants.

In an effort to address these problems in the field, we previously demonstrated that the introduction of flexible linear polymers, such as polyethylene glycol (PEG) and polycaprolactone (PCL), into GAP-based propellant formulations improved the mechanical and low-temperature properties of the propellant.⁴⁻⁶ Another approach has involved using HTPB, which displays excellent mechanical and low-temperature properties, as an initiator for the cationic polymerization of epichlorohydrin, a polymeric precursor to GAP.^{7,8}

We prepared a GAP-PB-GAP triblock copolymer according to the reported procedures; however, the reaction conditions failed to yield the triblock copolymer because the reactants appeared to become entangled (“gelated”) during the azidation reaction of the polyepichlorohydrin (PECH)-PB-PECH. Here, we investigated the causes underlying the entanglement during the azidation reaction. The triblock copolymer (PECH-PB-PECH) prepared by the cationic polymerization of ECH was characterized using precipitation methods, ¹H nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC).

Experimental

Cationic Ring-Opening Polymerization of Epichlorohydrin. Polymerization of ECH (purchased from Sigma-Aldrich, 99%) was carried out using HTPB (obtained from Atochem, R-45M) as an initiator in the presence of the Lewis acid (BF₃OEt₂ from Sigma-Aldrich, 99%) catalyst system. Under a N₂ atmosphere, BF₃OEt₂ (0.2 mL) was added to the mixture containing HTPB (2,810 g/mol, 20 g) and dichloromethane (150 mL, Sigma-Aldrich, 99%) at 13 °C, and the reaction was stirred for 2 h. ECH (20 g) was then added dropwise to the reaction mixture with cooling at 6.9 °C for 2 h. The polymerization reaction was accomplished by cooling at 6.9 °C for 5 h, followed by cooling at 16 °C overnight. After polymerization, the reaction was quenched with distilled water. The product mixture was washed with distilled water and a 5% sodium bicarbonate solu-

tion. The solvent was removed by rotary evaporation. The final polymeric products were separated using a fractional precipitation method. Finally, the PECH-PB-PECH triblock copolymer was obtained in a yield of 73%.

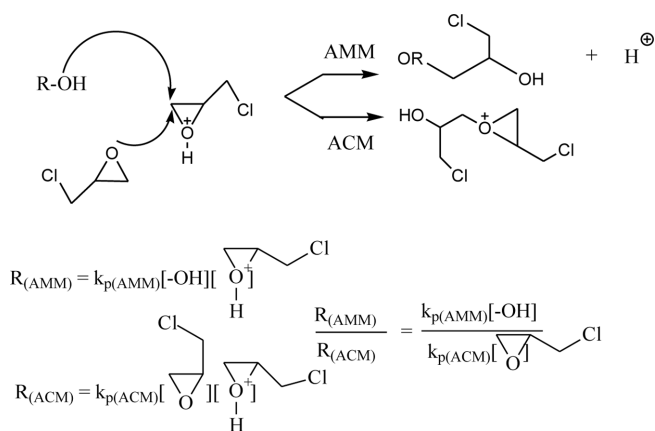
Azidation of the PECH-PB-PECH Triblock Copolymer. PECH-PB-PECH (25 g) was dissolved in DMSO (150 mL, Sigma-Aldrich, 99%) in a round bottom flask at 80 °C, and sodium azide (21.5 g, SAMCHEM Chemical, 99%) was slowly added. After heating to 105 °C, the reaction was allowed to proceed overnight.

Characterization of the PECH-PB-PECH. ¹H NMR spectra of PECH-PB-PECH were recorded using an ADRIAN spectrometer operated at 400 MHz. CDCl₃ (Sigma-Aldrich, 99%) was used as the solvent. The molecular weight was measured by size exclusion chromatography (Waters 2690) using Styragel HR-1, HR-2, HR-3, and HR-4 columns and polybutadiene as a standard.

Results and Discussion

Cationic Polymerization of Epichlorohydrin. Epichlorohydrin was catalytically polymerized by applying an activated monomer mechanism (AMM) to a telechelic polymer alcohol initiator, rather than by using an active chain-end mechanism (ACM) to suppress the formation of oligomers. As shown in Scheme 1, the polymerization reaction followed the AMM, provided that the concentration of the monomer was maintained at a low level through the slow addition of monomer to the reacting mixture of the alcohol and Lewis acid catalyst.

In our earlier study of the synthesis of low molecular weight (<1000 g/mol) GAP, a sudden exothermic reaction was



Scheme 1. Mechanisms underlying the cationic ring-opening polymerization reaction.

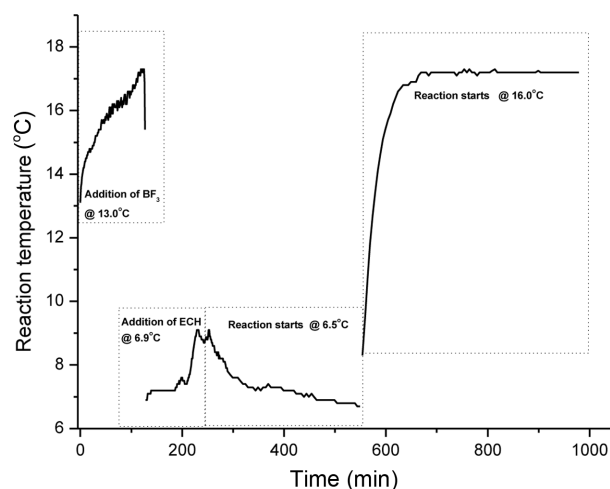


Figure 1. Temperature profile measured during the polymerization of ECH initiated by HTPB.

Table 1. Characteristics of the Triblock Copolymer Obtained Using the Fractional Precipitation Method

No.	γ	Amount (g)	M_n (g/mol) ^a	PDI	Ratio of copolymer ^b (PB:PECH)
1	0.75	26.6	5460	2.46	61:39
2	1.38	2.7	3593	1.94	36:64

^aMeasured by GPC using a polybutadiene standard.

^bCalculated by ¹H NMR.

observed during either the polymerization or the addition of ECH. The exothermic reaction was prevented by fractionally adding the monomer at low temperatures.⁹

Unlike the preparation of low-molecular weight polyepichlorohydrin, the HTPB-initiated polymerization of epichlorohydrin did not display a serious exothermic reaction leading to the overflow of the reactant mixture. As shown in Figure 1, only slightly exothermic reactions were observed during both the HTPB pre-initiation steps and the Lewis acid catalytic steps during the continuous slow addition of monomer.

After the ECH polymerization reaction, the PECH-PB-PECH triblock copolymer was separated from the resulting polymers containing unreacted HTPB and homo-PECH by the fractional precipitation method (solvent: chloroform, nonsolvent: methanol). Fractional precipitation methods are useful for separating a high molecular weight polymer from a mixture of polymers having a variety range of molecular weights. This method is frequently used to prepare multi-arm star polymers through anionic living polymerization reactions to yield a polydispersity of less than 1.1. In this study, the polydispersity of the HTPB diol initiator was about 2.2 because the HTPB

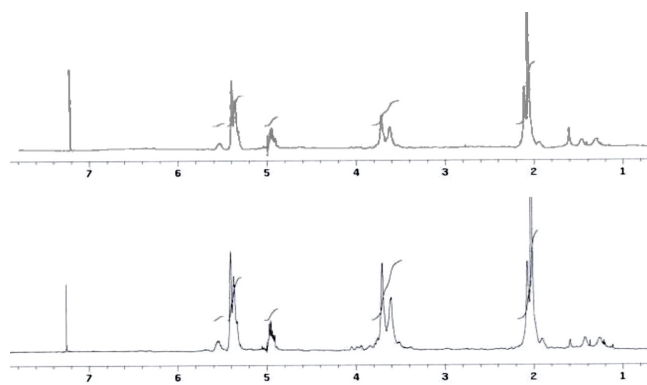


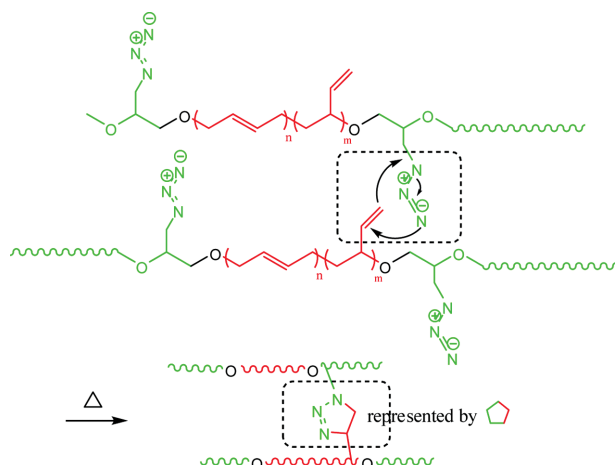
Figure 2. ¹H NMR spectra of the PECH-PB-PECH triblock copolymers precipitated at $\gamma=0.75$ (above) and 1.38 (below), respectively.

was prepared by a free radical polymerization. The polydispersity of PECH-PB-PECH could not, therefore, be as narrow as the polydispersity of the polymers obtained by an anionic living polymerization, even though ECH had been polymerized by a cationic polymerization reaction. As shown in Table 1, the triblock copolymer was characterized as having broad range of the nonsolvent-to-solvent (γ) volume ratio (0.75-1.38). A significant amount of the triblock copolymer precipitated at γ values near 0.75. At $\gamma=1.38$, only a very small amount of the triblock copolymer was collected. This sample was characterized by a molecular weight lower than that of the triblock copolymer obtained at $\gamma=0.75$. We determined that this polymer was a triblock copolymer containing PECH and HTPB by characterizing the sample using ¹H NMR techniques (Figure 2).

Figure 2 shows the ¹H NMR spectra of the PECH-PB-PECH triblock copolymer collected using the precipitation method at $\gamma = 0.75$ and 1.38. The proton peaks corresponding to HTPB appeared at 1.3–1.5 (–CH₂–CH(CH=CH₂)–, 1,2-unit), 2.1 (–CH₂–CH=CH–CH₂–, 1,4-unit), and 4.8–5.6 ppm (protons corresponding to the double bond in the 1,4- and 1,2-units). The peaks (–CH₂–CH(CH₂–Cl)–O–) at 3.4–3.8 ppm corresponded to protons in the PECH group.

Figure 2 compares the proton peaks in HTPB. The proton signal intensities of the proton peaks in PECH at $\gamma=1.38$ exceeded the intensities obtained at $\gamma=0.75$, indicating that ECH was initiated at both ends of HTPB in lower molecular weight fraction.

Azidation of the PECH-PB-PECH Triblock Copolymer. As reported elsewhere, the triblock copolymer was azidized (in an S_N2 reaction) at high temperatures; however, unlike previous reports describing azidation reactions involving this type



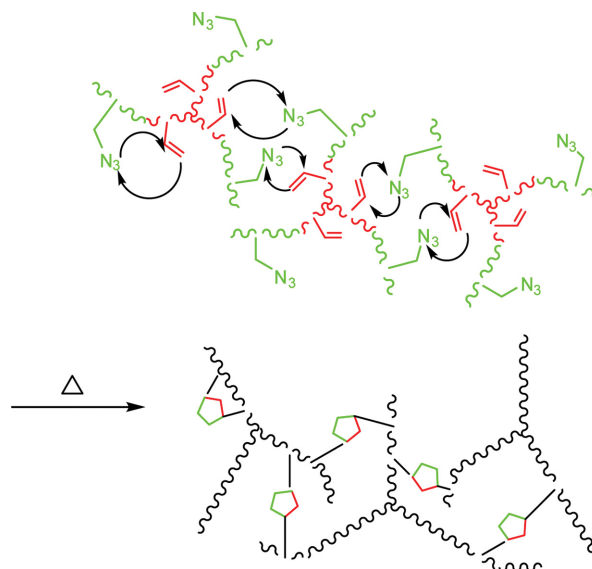
Scheme 2. 1, 3-dipolar cycloaddition between azide within GAP and a double bond of the 1, 2-unit in the polybutadiene.

of block copolymer, GAP-PB-GAP could not be successfully prepared through the azidation of PECH-PB-PECH. The failure of this reaction was attributed to the entanglement formation that occurred during azidation at high temperatures. In an effort to reduce the extent of entanglement and prevent the sudden azidation of PECH-PB-PECH, the nucleophile, sodium azide (NaN₃), was added very slowly to the PECH-PB-PECH solution. This approach was not effective in suppressing entanglement during the azidation reaction.

The most-likely cause of this entanglement was the 1,3-dipolar cycloaddition between the double bond in the 1,2 unit of HTPB and the azide group, which had replaced the chlorine group in the epichlorohydrin unit, leading to the formation of a triazoline group between the interpolymer chains or intrapolymer chains, as shown in Scheme 2. A triazoline group via a 1,3-dipolar cycloaddition of an azide and an alkene maybe readily formed if this reaction is carried out at high temperatures.¹⁰ In general, high temperatures and a reaction period exceeding one day are necessary for completing the azidation of PECH.¹

The HTPB initiator used in this study was commercially available under the trade name of R-45M. The hydroxyl functionality of this HTPB was in the range of 2.2 to 2.4, and the 1,2-unit (vinyl) provides a crosslinking site that accounts for nearly 20% of the polybutadiene microstructure (trans: 60%, cis: 20%). As shown in Scheme 3, an inter-cycloaddition reaction between the polymer chains most likely occurred during the azidation of PECH as well as the intra-cycloaddition reaction within a polymer chain.

On the other hand, as described in the introduction section,



Scheme 3. The inter- and intramolecular linking of the GAP-PB-GAP chains.

the successful azidation of PECH-PB-PECH has been reported previously. Our work is distinct from previous studies with respect to the type of HTPB used as the initiator. Although the characteristics of the HTPB used by others were not reported, the low hydroxyl functionality (<2.0) and the small vinyl content relative to the corresponding properties of HTPB (R-45M) appear to have prevented entanglement in the previously described azidation reactions of the triblock copolymers.

Conclusions

A hydroxyl-terminated PECH-PB-PECH was prepared through a cationic ring-opening polymerization of ECH using HTPB as the initiator. Unlike the polymerization of very low molecular weight PECH, a sudden exothermic reaction was not observed here. The triblock copolymer was obtained from the product mixture using a fractional precipitation method. Although previous reports describe the preparation of the corresponding copolymer (GAP-PB-GAP) through the azidation of the PECH-PB-PECH, this product was not obtained here because the partly and fully azidated PECH-PB-PECH reactants were heavily entangled during the azidation reaction at high temperatures. Further studies of the preparation of GAP-PB-GAP will be focused on the suppression of entanglement of PECH-PB-PECH during azidation by preparing hydroxyl-terminated polybutadiene having a very low molecular weight distribution and a very low vinyl content, and by conducting the azidation reaction at low temperatures.

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