

Cyclization of butadiene rubber with Lewis acid/cocatalyst systems

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Cyclization of butadiene rubbers by different types of Lewis acid catalysts and cocatalysts such as some organic halides has been investigated. The cyclization process was followed by physical and spectroscopic measurements. The cyclization process of butadiene-styrene rubber (SBR) was found to be achieved by using aluminium chloride as the catalyst and benzyl chloride as cocatalyst. The change in viscosity of cyclized products depends mainly on the concentration of the cocatalysts used. Thermal analysis by differential scanning calorimetry (d.s.c.) for cyclized SBR samples which cyclized under different conditions showed that the area under an endotherm is determined by the strength of the segment branches and heat of melting. The cyclization of *cis*-1,4-polybutadiene (BR) in the presence of aluminium chloride as catalyst and trichloroacetic acid as cocatalyst was carried out and found to be dependent on the concentrations of both.

(Keywords: butadiene; Lewis acid; cocatalyst; rubbers)

INTRODUCTION

Alkyl aluminium compounds are effective grafting agents for halogenated polymers such as PVC, neoprene, chlorinated polyethylene etc.¹ Similarly, the cyclization of butadiene rubbers can be achieved in the presence of a second component, termed a cocatalyst, such as some organic halides and trichloroacetic acid.

The cyclization reaction does not occur readily. The mechanism of cyclization is still unknown². This study aimed to obtain cyclized styrene-butadiene rubber which can be separated easily. The cyclization of *cis*-1,4-BR was carried out in the presence of Lewis acid catalysts and with some organic halides as cocatalysts. The cyclized butadiene rubbers are expected to be useful as photoresists with high photosensitivity^{3,4}.

EXPERIMENTAL

Commercial samples of polybutadiene-styrene SBR (24% styrene and 76% butadiene) and polybutadiene BR (96% *cis*, 4% *trans* and vinyl contents) were supplied by Bayer Co., West Germany. Lewis acids such as titanium chloride and aluminium chloride (BDH) were used as received. Organic halogen compounds such as trichloroacetic acid and benzyl chloride were of pure grades and used without further purification. Pure grade solvents such as methanol, toluene and benzene were used. The cyclization reaction of polybutadiene-styrene was carried out at a concentration 0.042 mol monomer unit/l in 40 ml toluene at 40°C. The Lewis acid catalysts and cocatalysts were added at concentrations 10⁻³ equivalent to the concentration of polymer. At the end of the cyclization reaction, the solution was filtered through a sintered glass filter G4. Methanol as non-solvent was added to the filtrate to precipitate the cyclized product. I.r. spectroscopic measurements were made using a Pye Unicam SP 2060 double beam spectrometer for polymer films cast from benzene on sodium chloride plates; u.v. spectroscopic measurements were made using a Perkin

Elmer Lambda 3B spectrometer with a 1 cm cell. Thermal analysis of solid cyclized polymer was carried out by differential scanning calorimetry (d.s.c.) (DSC 111 Setram, Lyon, France).

The viscosities η_{rel} of polymer solutions were measured at the concentration 0.26 g/dl at 30°C in toluene using an Ubbelohde dilution viscometer by applying the relationship:

$$\eta_{rel} = \frac{t_1 \text{ solution}}{t_0 \text{ solvent}}$$

RESULTS AND DISCUSSION

Cis-1,4-polyisoprene is cyclized by Lewis acid catalysts such as stannic chloride and aluminium chloride^{3,4}. In this study, the cyclization of butadiene rubbers by these catalysts in the presence of some organic halides such as allyl chloride, benzyl chloride and trichloroacetic acid was found to result in cyclized polymers without gel formation. The results are shown in Table 1. With AlCl₃ as catalyst and CCl₃COOH as cocatalyst (experiments 1, 2 and 3), no appreciable change occurred in relative viscosity compared with that of the unreacted SBR. This may be due to the absence of cyclization. With C₆H₅CH₂Cl as cocatalyst the relative viscosity increased, and a higher cyclization was reached at concentrations 9.7 × 10⁻⁴ mol of AlCl₃ and 7.9 × 10⁻⁴ mol of C₆H₅CH₂Cl where a powder is obtained. However, the decrease in concentration of the cocatalyst greatly affected the state of cyclized products when TiCl₄ as catalyst and CCl₃COOH as cocatalyst were used. This is clear from the viscosity data (samples 9-13) in Table 1. Thus, the concentration of the cocatalyst affected the viscosity of the cyclized products and this is explained as a result of changes in their microstructure. The cyclization process of SBR by aluminium chloride in the presence of trichloroacetic acid was investigated. As shown in the infra-red spectra of cyclized SBR (Figure 1), the microstructure of the cyclized rubber changed and was

Table 1 Cyclization reaction of SBR^a

Catalyst	mol	Cocatalyst	mol	Reaction time (min)	η_{rel}^b Toluene	Product
AlCl ₃	1.49×10^{-3}	CCl ₃ COOH	1.22×10^{-3}	40	1.43	Rubber
	4.4×10^{-3}	CCl ₃ COOH	1.22×10^{-3}	40	1.45	Rubber
	1.49×10^{-3}	None	—	40	1.43	Rubber
	9.7×10^{-4}	C ₆ H ₅ CH ₂ Cl	7.9×10^{-4}	40	—	Powder
	9.7×10^{-4}	C ₆ H ₅ CH ₂ Cl	1.6×10^{-3}	40	1.8	Rubber
	4.9×10^{-4}	C ₆ H ₅ CH ₂ Cl	1.6×10^{-3}	40	1.54	Rubber
	9.7×10^{-4}	C ₆ H ₅ CH ₂ Cl	0.4×10^{-3}	40	1.89	Rubber
	4.9×10^{-4}	C ₆ H ₅ CH ₂ Cl	0.8×10^{-4}	40	1.84	Rubber
	TiCl ₄	9.1×10^{-4}	CCl ₃ COOH	2.6×10^{-4}	40	1.64
9.1×10^{-4}		CCl ₃ COOH	5.3×10^{-4}	40	1.89	Rubber
9.1×10^{-4}		CCl ₃ COOH	7.9×10^{-4}	40	—	Partly gelled
9.1×10^{-4}		CCl ₃ COOH	1×10^{-3}	40	—	Hard rubber
9.1×10^{-4}		CCl ₃ COOH	1.3×10^{-3}	40	—	Hard rubber
2.6×10^{-3}		None	—	40	—	Hard rubber
1.1×10^{-3}		None	—	40	—	Partly gelled
0.53×10^{-3}		CCl ₃ -COOH	2.5×10^{-4}	40	1.89	Rubber
3.3×10^{-3}		None	—	40	1.78	Rubber
6.7×10^{-4}		CCl ₃ -COOH	2.5×10^{-4}	40	1.54	Rubber

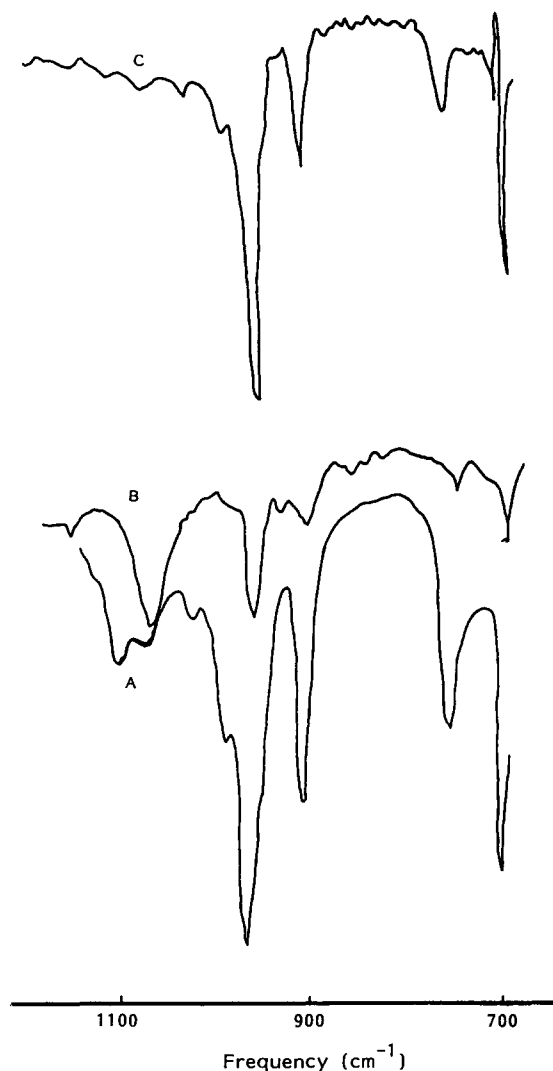
^a 4.2×10^{-2} mol monomer unit l⁻¹ in 40 ml toluene at 40°C^b η_{rel} of untreated SBR = 1.49

Figure 1 Infra-red spectra for polybutadiene-styrene and its related cyclized products using the system AlCl₃/CCl₃COOH: (A) uncyclized SBR, (B) AlCl₃ (1.49×10^{-3} M)/CCl₃COOH (1.2×10^{-3} M) and (C) AlCl₃ (4.4×10^{-4} M)/CCl₃COOH (1.2×10^{-3} M)

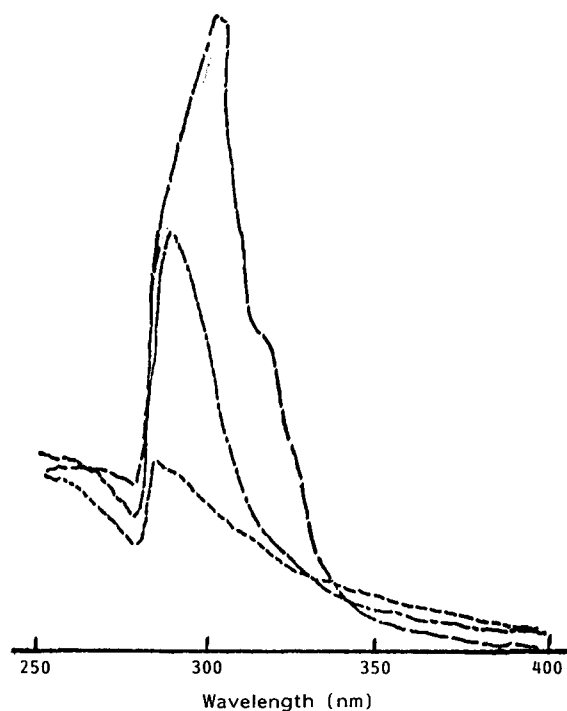


Figure 2 Electronic absorption spectra of starting polybutadiene-styrene: (----), uncyclized SBR; (- - -), SBR cyclized product using the system TiCl₄ (5.3×10^{-3} M)/CCl₃COOH (2.6×10^{-4} M); (—), SBR cyclized product using the system AlCl₃ (4.4×10^{-4} M)/CCl₃COOH (1.2×10^{-3} M) in toluene (0.8 g/dl)

not identical to the uncyclized rubber. Further studies were carried out on the structure of the cyclized rubber using u.v. spectroscopy as shown in Figure 2. It was found that the cyclization of SBR slightly affects the position of λ_{max} in the region of 300–330 nm.

The cyclization of SBR was also investigated with titanium chloride as catalyst and in the absence and presence of trichloroacetic acid as cocatalyst. In Figure 3, it was found that new absorption peaks appeared in the region between 700–900 cm⁻¹ and at 865 and 755 cm⁻¹.

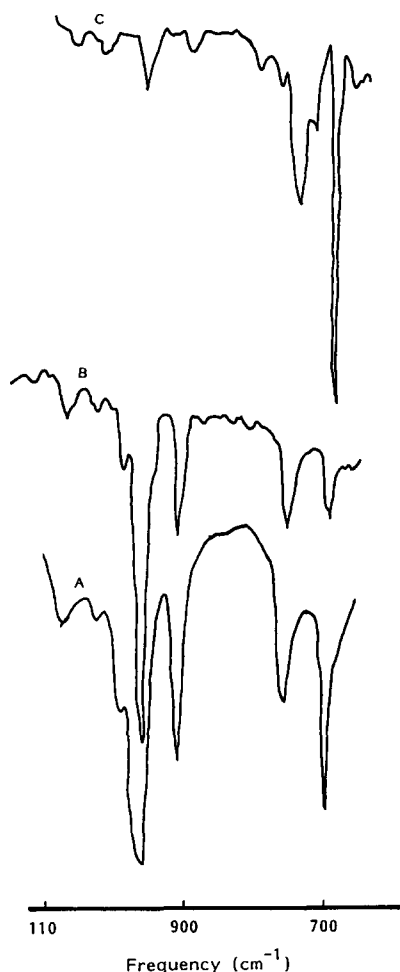


Figure 3 Infra-red spectra for polybutadiene-styrene and its cyclized products using the system $\text{TiCl}_4/\text{CCl}_3\text{COOH}$: (A) uncyclized SBR; (B) TiCl_4 ($1.1 \times 10^{-3} \text{ M}$)/ CCl_3COOH ($2.5 \times 10^{-4} \text{ M}$) and (C) TiCl_4 ($5.3 \times 10^{-3} \text{ M}$)/ CCl_3COOH ($2.5 \times 10^{-4} \text{ M}$)

These may be due to the C-H deformation (out of plane) of the cyclized products. These peaks confirmed the occurrence of cyclization as known before for the cyclization of *cis*-1,4-BR².

It was found in the literature that the cyclization process occurs as an intramolecular reaction in the presence of H^+ and involves protonation and the addition of the resulting carbonium ion to an adjacent double bond to form a six membered ring. The mechanism of cyclization of natural rubber and *cis*-1,4-polyisoprene was suggested previously⁵. However, in the case of the cyclization of BR and SBR rubbers, this mechanism is not valid, because in this study the infra-red spectra of the cyclized products did not confirm the presence of the CH_2 groups of six membered rings. The CH_2 group should give two tentative peaks at $1000\text{--}1055 \text{ cm}^{-1}$ and $1005\text{--}952 \text{ cm}^{-1}$.

The cyclization of SBR in the presence of AlCl_3 and TiCl_4 as catalysts and benzyl chloride as cocatalyst was conducted. In the infra-red spectra of cyclized rubber (Figures 4 and 5), new peaks appeared at 840 and 730 cm^{-1} and the change was observed in the microstructure of the cyclized rubber. The appearance of new peaks at these regions is mainly due to the presence of a C-H bond, and the peaks become smaller or larger according to the concentration of the cocatalyst used (Figures 4 and 5).

The d.s.c. diagrams of the uncyclized and cyclized SBR rubbers between 233–680 K are shown in Figure 6. The observed endotherms reflect the melting of branch segment domains. The areas under the melting endotherms are related to the strength of the segment branches. The observed endotherms with multiple peaks as in the case of Figure 6b reflects the sequential melting. Consequently, the change in nature of the repeat units in the chain and branching all influence the physical properties of the products.

In another trial, the cyclization process of *cis*-1,4-BR was investigated using AlCl_3 as catalyst and trichloroacetic acid as cocatalyst. First, the concentration of the cocatalyst was changed. The cyclization process was carried out as mentioned before in the case of SBR (see Table 1). Comparison of the infra-red spectra of the uncyclized and cyclized rubbers (Figure 7) showed that new peaks appeared clearly in the finger print region and their presence is considered to be a good indication of the occurrence of cyclization². In the second case, the concentration of the catalyst was changed. The results summarized in Figure 8 showed a new absorption peak in the region $800\text{--}900 \text{ cm}^{-1}$, and this means that the microstructure of the polymer was changed. It was found

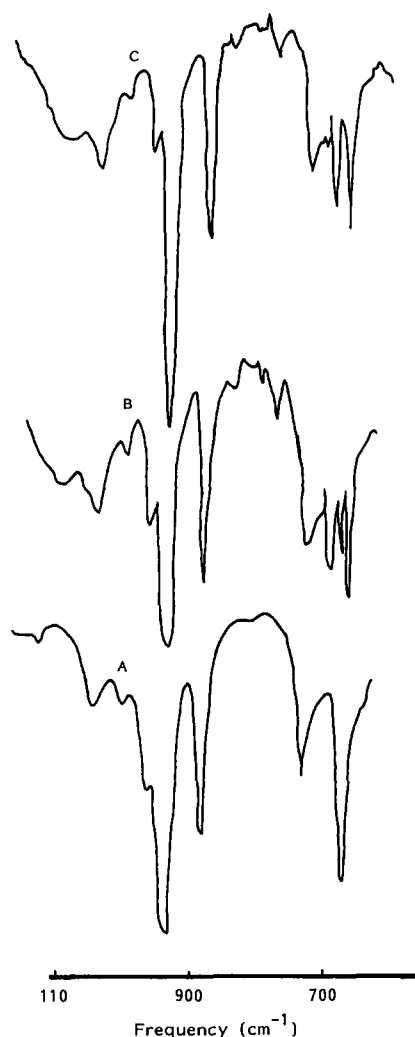


Figure 4 Infra-red spectra for polybutadiene-styrene and its cyclized products using the system $\text{AlCl}_3/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$: (A) uncyclized SBR; (B) AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ($7.9 \times 10^{-4} \text{ M}$) and (C) AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ($1.6 \times 10^{-3} \text{ M}$)

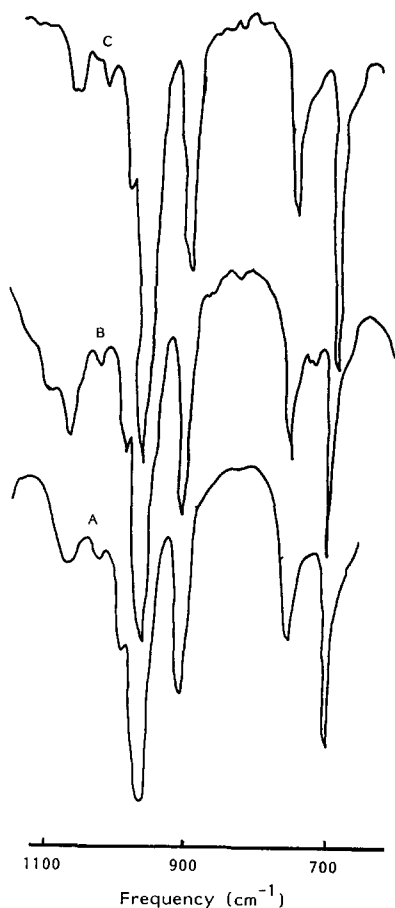


Figure 5 Infra-red spectra for polybutadiene-styrene and its cyclized products using the systems $\text{AlCl}_3/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{TiCl}_4/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$: (A) uncyclized SBR; (B) AlCl_3 ($4.9 \times 10^{-4} \text{ M}$)/ $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ($1.6 \times 10^{-3} \text{ M}$) and (C) TiCl_4 ($1.1 \times 10^{-3} \text{ M}$)/ $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ($1.6 \times 10^{-3} \text{ M}$)

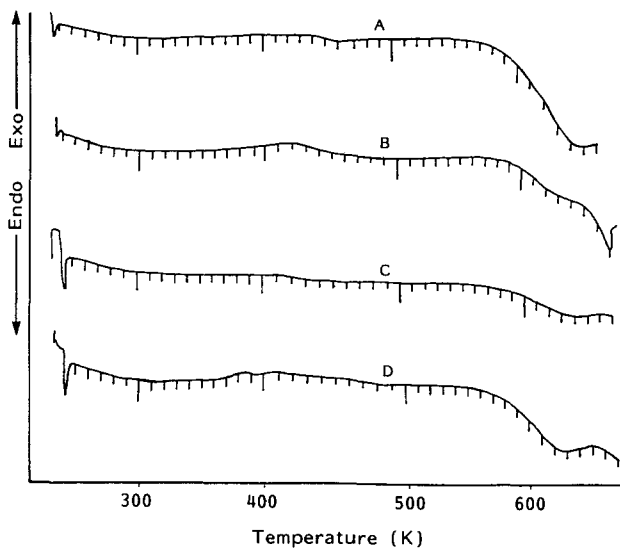


Figure 6 D.s.c. diagrams of starting polybutadiene-styrene and its cyclized products: (A) uncyclized SBR; (B) TiCl_4 ($5.3 \times 10^{-3} \text{ M}$)/ CCl_3COOH ($2.6 \times 10^{-4} \text{ M}$); (C) AlCl_3 ($4.4 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($1.2 \times 10^{-3} \text{ M}$) and (D) AlCl_3 ($1.49 \times 10^{-3} \text{ M}$)

that the u.v. spectra of the cyclized BR has a higher sensitivity than the uncyclized BR, as shown in Figure 9.

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

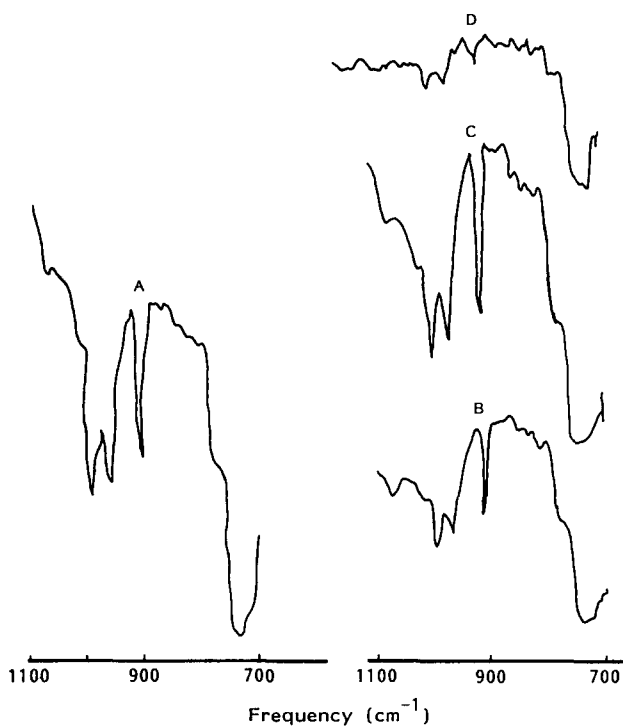


Figure 7 Infra-red spectra for polybutadiene and its cyclized products using the system $\text{AlCl}_3/\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$: (A) uncyclized SBR; (B) AlCl_3 ($4.8 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($1 \times 10^{-2} \text{ M}$); (C) AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($1 \times 10^{-2} \text{ M}$) and (D) AlCl_3 ($1.9 \times 10^{-3} \text{ M}$)/ CCl_3COOH ($1 \times 10^{-2} \text{ M}$)



Figure 8 Infra-red spectra for polybutadiene and its cyclized products using the system $\text{AlCl}_3/\text{CCl}_3\text{COOH}$: (A) uncyclized; (B) AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($5.2 \times 10^{-3} \text{ M}$); (C) AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ CCl_3COOH (0.01 M) and (D) AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($2 \times 10^{-3} \text{ M}$)

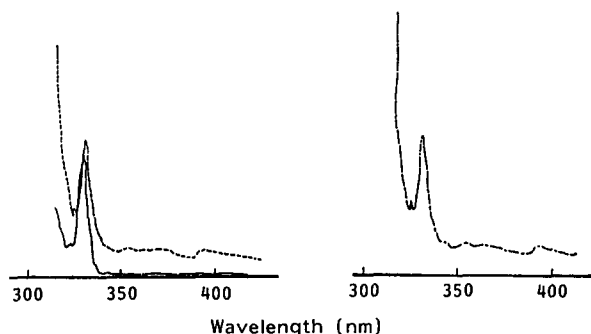
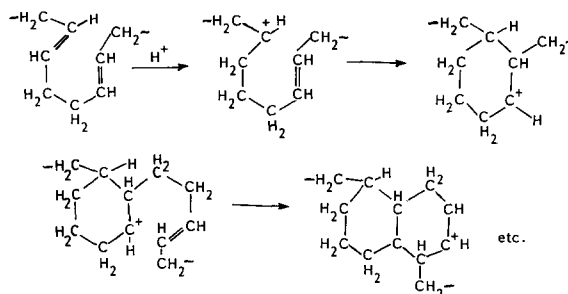


Figure 9 Electronic absorption spectra of starting polybutadiene and its cyclized products using the system $\text{AlCl}_3/\text{CCl}_3\text{COOH}$: (—), uncyclized BR; (----), AlCl_3 ($4.8 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($1 \times 10^{-2} \text{ M}$) and (- · - · -), AlCl_3 ($9.7 \times 10^{-4} \text{ M}$)/ CCl_3COOH ($2 \times 10^{-3} \text{ M}$) in benzene (0.8 g dl^{-1})

intramolecular reaction for macromolecules is more favourable; that is the cyclization is neither a scission of the polymer nor an intermolecular reaction². However, in this study the cyclization process was followed by i.r. spectroscopy and, if the cyclization occurred only by intramolecular reaction, the absorption of the double bond would be decreased, in addition to the appearance of a new peak for the C-H deformation in the range $700\text{--}800 \text{ cm}^{-1}$. The cyclization of butadiene rubbers in presence of H^+ and/or $\text{C}_6\text{H}_5\text{CH}_2^+$ in presence of Friedel-Crafts catalysts (e.g. aluminium chloride and stannic chloride) which were used in the present study can proceed as in the following:



Scheme 1

This mechanism explains the appearance of the absorption of the C-H deformation in the range $700\text{--}800 \text{ cm}^{-1}$.

CONCLUSION

The cyclization of butadiene rubbers has been investigated in detail. Cyclization can be achieved by using Lewis acid catalysts and cocatalysts such as some organic halides. Experiments to discover the structure of the resulting cyclized rubber threw some light on the nature of the cyclization reaction. Cyclization does not occur readily according to reports. The mechanism of cyclization is still unknown.

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