1-Chlorobutadiene–Butadiene Rubber.
IV. Increasing the Hydroxyl Group Content in the Rubber

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Synopsis

The hydroxyl group content in 1-chlorobutadiene–butadiene rubber (CB–BR) was increased by the following two methods: (1) heating of the CB–BR latex to hydrolyze the unstable chlorine in CB–BR and (2) introduction of hydroxyl by the Menschutkin-type reaction between 2-dimethylaminoethanol (DMAE) and the chlorine in CB–BR. By heating the latex at 70°C for 12 hr, 55% chlorine was hydrolyzed to result in a marked increase in hydroxyl group content in CB–BR. This may be explained by the microstructure of the 1-chlorobutadiene (CB) units in CB–BR, i.e., at least 55% chlorine is situated in the CB units of the 1,4-configuration. Heat-treated CB–BR was found to contain a small amount of conjugated triene structure by UV spectroscopy, which indicates that elimination of some unstable chlorine as hydrogen chloride occurs during latex heating. By reaction with DMAE, 44% chlorine was converted into hydroxyl in toluene at 27°C. CB–BR compounded with DMAE does not suffer from gelation by milling on an open roll. Thus, by these methods, high molecular weight butadiene rubber having various concentrations of hydroxyl groups is obtained.

INTRODUCTION

In a previous paper,[1] the hydroxyl groups in 1-chlorobutadiene–butadiene rubber obtained by emulsion polymerization (CB–BR) were determined by ultraviolet spectroscopy (UV) and allowed to react with tolylene diisocyanate to afford CB–BR vulcanizates. The hydroxyl group probably results from hydrolysis of the active chlorine in CB–BR, since it is difficult to control the hydrolysis during the purification and drying of the polymer, thence the hydroxyl group content in CB–BR.[1] In addition, the hydroxyl group content was too low to enter into various chemical reactions with CB–BR in most cases.[1]

In this work, some approaches to increase the hydroxyl group content in CB–BR were developed, and experimental conditions for obtaining the CB–BR having a suitable hydroxyl group content were explored. At first, CB–BR latex was heated to promote hydrolysis. Latexes of halogen-containing polymers such as poly(vinyl chloride),[2] polychloroprene,[2] and poly(vinylidene chloride)[3] are destroyed slowly by the evolution of hydrogen chloride due to the hydrolysis of chlorine in these polymers. Since CB–BR should be synthesized with a low 1-chlorobutadiene (CB) content in the monomer feed in order to avoid gelation, the application of heat for the hydrolysis of CB–BR latexes may be favorable for increasing the hydroxyl group content without destruction of the latex.

Secondly, the reaction of 2-dimethylaminoethanol (DMAE) with CB–BR was attempted to introduce hydroxyl groups into CB–BR. The reaction of an amine with an organic halide to form a quarternary ammonium salt is known as the

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Menschutkin-type reaction, and some studies on the application of this reaction to polymer modifications have been made.[4–7]

EXPERIMENTAL

Materials

CB–BR Latex

Emulsion copolymerizations of CB and butadiene (Bd) were carried out as reported earlier.[8] The ratio of CB/Bd in the monomer feed was 5/95 by weight. After the polymerization, residual Bd was removed by bubbling nitrogen gas. The latex was stored at room temperature under a nitrogen atmosphere. The solid content in the latex was nearly 20%.

DMAE. Guaranteed reagent DMAE was distilled (bp 134°C, lit.[9] 135°C) prior to use.

Coagulating Solution

A methanol solution of di-n-butyltin dilaurate (1%) and 2,6-di-t-butyl-p-cresol (0.2%) was employed to coagulate the latex.

Procedures

Hydrolysis by Heating the Latex

In a series of three flasks, 300 ml CB–BR latex adjusted to pH 13.0 was kept at 50, 70, and 90°C, respectively, with stirring under an atmosphere of nitrogen. After fixed time intervals, 10-ml aliquots of the polymerization solution were withdrawn by syringe, followed by coagulation in methanol. The recovered polymers were washed, dried under vacuum at room temperature for three days, and reprecipitated from benzene–methanol.

Reaction of CB–BR with DMAE

The following two methods were adopted: (1) In the solution method; 2 g CB–BR and 0.24 g DMAE were dissolved into 20 ml toluene and allowed to react at 27°C under stirring. After fixed time intervals, aliquot samples of the reaction solution were withdrawn, and the recovered polymers were subjected to UV measurements in order to determine the hydroxyl group content. (2) In the compounding method; 100 g CB–BR was compounded with 6.2 g DMAE by using an open roll, and the compound was pressed at 100°C for 60 min, followed by pressing at 150°C for 15 min to remove the residual DMAE. After the treated CB–BR was dissolved in benzene, the solution was filtered through a 100-mesh wire gauze, and the gel fraction was determined. The sol fraction was subjected to UV analysis.

Determination of Hydroxyl Group Content

The hydroxyl group content in CB–BR was determined according to the UV method reported in a previous paper.[1]

Viscosity and DSC Measurements

Intrinsic viscosity was measured in toluene at 25.9°C with an Ubbelohde-type viscometer. Differential scanning calorimetry (DSC) was carried out on a Rigaku DSC Instrument (Rigaku Denki Co.).

RESULTS AND DISCUSSION

Hydrolysis of Chlorine by Heating CB–BR Latex

In Figure 1, the influences of the heating time of CB–BR latex at 70°C on the hydroxyl group and chlorine contents in the CB–BR are shown. As the heating time increased, the chlorine decreased and the hydroxyl group increased. Moreover, both contents attained asymptotic values after 12 hr. These findings suggest that the increase in hydroxyl group content is attributable to the hydrolysis of chlorine in the CB unit of CB–BR.

The attained hydrolysis percent under these conditions was estimated as follows:

$$\% \text{ hydrolysis} = \frac{[OH]}{[Cl] + [OH]} \times 100 \tag{1}$$

where [OH] and [Cl] are, respectively, the hydroxyl group and chlorine concentrations in mol/g CB–BR. The asymptotic value of the percent hydrolysis was found to be 51%. This means that about one half the amount of chlorine in the CB unit is susceptible to hydrolysis simply by heating the latex at 70°C. Figure 1 also shows that the CB–BR before heating contained about 1×10^{-4} mol/g hydroxyl group. This may be due to the inevitable hydrolysis during the polymerization and the storage of latex at room temperature for about four days, in addition to the procedure for purification of CB–BR.[1]

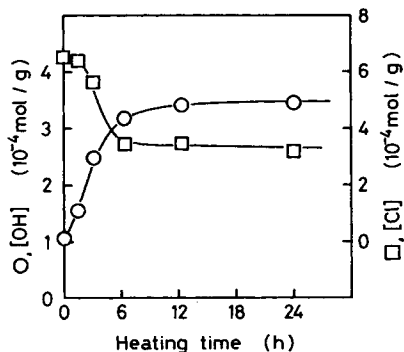The temperature dependence of the hydrolysis is indicated in Figure 2. The

Fig. 1. Hydroxyl Group and chlorine contents in CB–BR obtained by heating the latex at 70°C: [OH] before heating = 1.1 × 10⁻⁴ mol/g; [Cl] before heating = 6.3 × 10⁻⁴ mol/g; (O) [OH]; (□) [Cl].
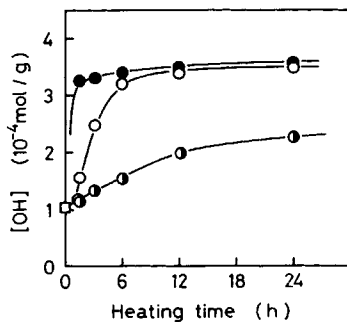
Fig. 2. Influence of heating time and temperature of latex on hydroxyl content: (□) without heating; (◑) heating at 50°C; (○) heating at 70°C; (●) heating at 90°C.

rate of hydrolysis at 50°C was relatively small, and the higher the reaction temperature the larger the rate. Both asymptotic hydroxyl contents at 70 and 90°C coincide well. The somewhat higher hydroxyl value obtained at 90°C might be attributed to a greater extent of hydrolysis than at 70°C, but seems to be within the limits of experimental errors.

DSC measurements were carried out on heat-treated CB–BR. The result is shown in Figure 3, together with that of the unheated CB–BR. The latter showed an exothermic peak at around 230°C, which can be assigned to the exothermic elimination of unstable chlorine to form hydrogen chloride in air.[10] The heat-treated CB–BR did not show this peak in DSC, because the unstable chlorine in the heat-treated CB–BR had been converted to hydroxyl by the application of heat.

These behaviors may be correlated with the microstructure of the CB unit in CB–BR. Four microstructures in the CB unit are considered, as shown below, i.e., 1,2-, cis-1,4-, trans-1,4-, and 3,4-structures:
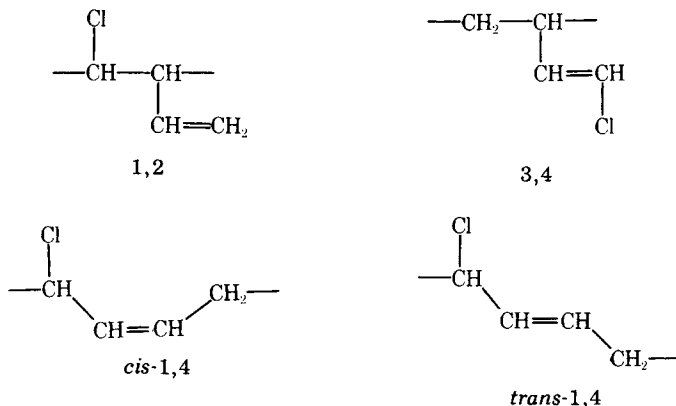
There are also cis and trans configurations for the 3,4-structure. Among chlorines in these five configurations, the ones attached to the cis- and trans-1,4-structures are assumed to be more reactive than the others, since chlorines are situated on an allylic position. On the other hand, chlorine bonded to vinyl is known to be relatively stable. Thus, there is no need to take the hydrolysis of the chlorine on the 3,4-structure into account. The chlorine located in 1,2-enchainment should show intermediate reactivity because of its β-position to

the carbon–carbon double bond. However, 1,2-addition of CB is considered practically impossible because 1,2-disubstituted ethylenes are reluctant to polymerize by free-radical initiators.[11] Winston et al.[12] reported the same result on poly(CB–co–styrene), and structural studies by us on the microstructure of the CB unit also seem to support this consideration.[13]

Thus, it may be concluded that only the chlorines of the *cis*- and *trans*-1,4-structures of the CB unit are hydrolyzed. Since about half of the chlorine was converted to hydroxyl in the emulsion copolymerization of CB with Bd, 1,4-addition of CB competes with 3,4-addition, and about half of the CB is present in 3,4-structure. This result is somewhat different from that of Winston et al.[12] They reported that almost all the CB units in poly(CB–co–styrene) obtained by radiation-induced polymerization were present in the 1,4-form.[12] However, our result obtained from the structural characterization of poly(CB–co–styrene) produced by free-radical initiators led to the conclusion that the CB unit consists of about 40% 3,4-structure and 60% 1,4-structure.[13] Therefore, the microstructure of the CB unit observed from the hydrolysis of CB–BR seems to be consistent with our structural characterization by means of infrared and H^1-NMR spectroscopies.[13]

Elimination of Chlorine by Heating the CB–BR Latex

Figure 4 indicates the correlation between the decreased chlorine content and the increased hydroxyl content in CB–BR when the latex is heated. In this figure, the value 7.7 corresponds to the sum of [OH] and [Cl], in 10^{-4} mol/g, i.e., the CB unit content in CB–BR. Therefore, if all the unstable chlorine were hydrolyzed, the observed value should be on the solid line in the figure. As seen, three samples having high hydroxyl content deviated from the straight line. The fact that the increased hydroxyl concentration formed by the hydrolysis is lower than the decreased concentration of active chlorine may be attributed to the elimination of chlorine which should have been converted into hydroxyl. The three samples with a high hydroxyl group content were, in fact, obtained by being kept at 70°C for a longer time.

The effect of heating time of the latex at 50°C on the UV spectra of CB–BR is shown in Figure 5, where, as the heating time becomes longer, the absorbances of the peaks in the 260–280 nm region become larger. These absorption maxima
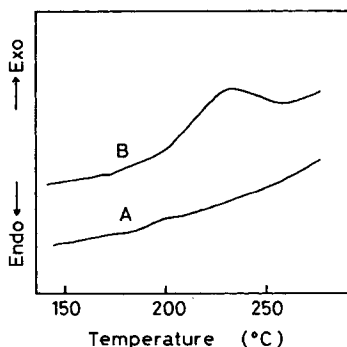

Fig. 3. DSC thermograms of heat-treated and unheated CB–BR measured in air: A, heat treated at 70°C for 12 hr; B, unheated.
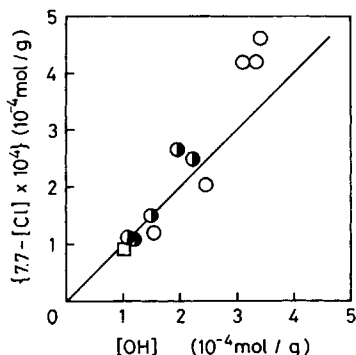
Fig. 4. Relationship between chlorine decreased by the application of heat to the latex and hydroxyl group content. Symbols are the same as in Fig. 2.
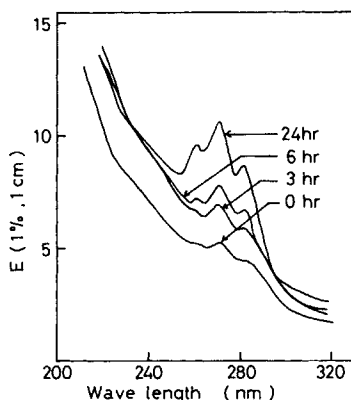

Fig. 5. UV spectra of heat-treated CB–BR at 50°C. Observed absorbance = E (1%, 1 cm) $\times C$; C = polymer concentration in cyclohexane, in g/100 ml.

are assumed to be due to conjugated triene structures caused by the elimination of hydrogen chloride, as shown in Table I.

From Figure 5 it is seen that the absorption maximum at 270 nm was exhibited by CB–BR prior to heating, though the intensity was much lower than that of the heat-treated ones. This shows the occurrence of hydrogen chloride elimination during the polymerization or the standing time after polymerization. As described above, only the chlorine on the 1,4-structure in the CB units appears to participate in this elimination reaction. Among the four diads containing CB units of 1,4-structure, I, II and IV (in Table I) are converted to the structure having a triene unit after the hydrogen chloride elimination, and polyene structures of higher conjugation result from III (see I′, II′, IV′, and III′ in Table I). Experimentally no absorption was detected in the visible region, even in the case of the CB–BR which showed the largest absorbance at 270 nm, thus suggesting the absence of diad III since conjugation higher than three shows an absorption maximum at a longer nanometer range than 300 nm. For example, 1,3,5,7-octatetraene, which seems to have a maximum at the shortest wavelength among the tetraenes, shows an absorption maximum at 290 nm.[14]

From the monomer reactivity ratios and the composition of the monomer feed, the monomer sequence distribution in the copolymer may be evaluated. The calculated values are indicated on the second column in Table I. According to

TABLE I
Addition Mode of Diad in CB–BR and Structure After Elimination of Hydrogen Chloride

Diad in CB–BR	Mol %ᵃ in CB–BR	Addition mode	Structure after elimination
—Bd—CB—	9.95	I: —CH₂—CH=CH—CH—CH—CH=CH—CH₂— (H, Cl; 1,4)	I': —CH₂—CH=CH—CH=CH—CH=CH—CH₂—
		II: —CH₂—C—CH=CH—CH₂— (H, Cl; CH=CH₂; 1,4 1,2)	II': —CH₂—C=CH—CH=CH—CH₂— (CH=CH₂)
		III: —CH—CH=CH—CH—CH—CH=CH—CH₂— (Cl; H, Cl; 1,4 1,4)	III': =CH—CH=CH—CH=CH—CH=CH—CH₂—
		IV: —CH₂—C—CH—CH=CH—CH₂— (H, Cl; CH=CHCl; 3,4 1,4)	IV': —CH₂—C=CH—CH=CH—CH₂— (CH=CHCl)
—CB—CB—	0.04		

ᵃ Calculated values from monomer feed (CB, 5 wt. %) and monomer reactivity ratios.[15] The rest (90.01%) is —Bd—Bd—diad.

these values, the diad —CB—CB— is present in very small amounts. We can ignore structures III and IV from this consideration. This conclusion was partly supported by the fact that structure III′ was not at all detected in the UV analysis of the heat-treated CB–BR. Accordingly, the peaks in Figure 5 are ascribable to the triene structures derived from the Bd–CB diad (I′ and II′ in Table I).

The absorption maxima and the molar absorptivities of the trienes have been reported, for example, for 1,3,5-hexatriene (λ_{max} = 258, log ϵ = 4.9)[16] and 2,4,6-octatriene (λ_{max} = 270, log ϵ = 4.6).[17] The concentration of the trienes was evaluated by assuming that ϵ is 30,000 at 270 nm. The calculation showed that about 5% of the total chlorine was eliminated while about 50% was hydrolyzed. So it may be concluded that the concentration of 1,4-CB in the CB units attained at least 55%, which is consistent with our unpublished results.[13]

Intrinsic Viscosity of CB–BR of Various Hydroxyl Contents

The intrinsic viscosity [η] of CB–BR was increased slightly by heating the CB–BR latex. For example, intrinsic viscosity of the original sample was 0.89 dl/g and that heated at 70°C for 12 hr was found to be 0.94 dl/g. Some intermolecular reactions might take place during the heating of the latex. Intermolecular elimination of hydrogen chloride is a candidate for these reactions.

Values of the Huggins constant k' were obtained in the determination of intrinsic viscosity from the equation

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C \tag{2}$$

where C is the concentration of the polymer, in dl/g. In Figure 6, the inverse of this value is plotted against the hydroxyl group content in CB–BR. Although the physical meaning of the Huggins constant is not yet fully explained, it has been found that the more highly branched the polymer, the larger is the Huggins constant.[18] From Figure 6 it seems that increasing the hydroxyl group in CB–BR tends to decrease the branches. Namely, CB–BR having a higher concentration of chlorine undergoes some reactions caused by unstable chlorine leading to the branched polymer, while the concentration of active chlorine available for such reaction is extremely decreased in CB–BR having a higher hydroxyl group content.
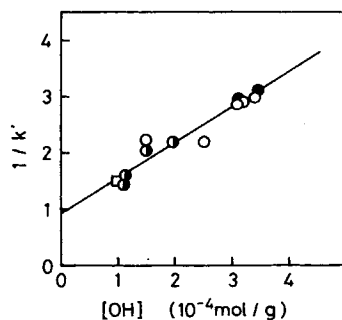

Fig. 6. Huggins coefficient k' and hydroxyl group content in CB–BR. Symbols are the same as in Fig. 2.
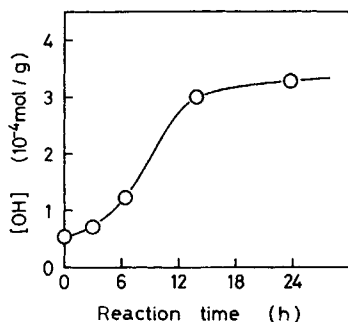
Fig. 7. Increase in hydroxyl group content of CB–BR by reaction with DMAE: [OH] before reaction = 0.55×10^{-4} mol/g; [Cl] before reaction = 7.1×10^{-4} mol/g; $[\eta]$ = 1.08 dl/g; solvent, toluene; temperature, 27°C.
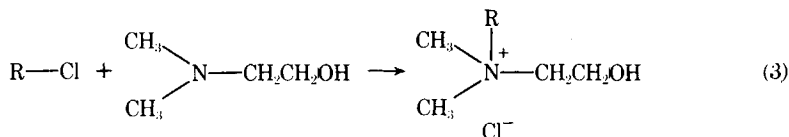
TABLE II
Effect of Compounding DMAE[a] on CB–BR Milling

	[OH], 10^{-4} mol/g	Gel fraction, %
Original CB–BR	0.6	0
Milled CB–BR without DMAE	1.1	71.1
Milled CB–BR with DMAE	1.3	0.6

[a] 2-Dimethylaminoethanol.

Increase in Hydroxyl Content by Reaction with DMAE

When CB–BR is allowed to react with DMAE, a hydroxyl group is introduced according to the following equation:

$$R-Cl \; + \; \overset{CH_3}{\underset{CH_3}{>}}N-CH_2CH_2OH \; \longrightarrow \; \overset{CH_3}{\underset{CH_3}{>}}\overset{\overset{R}{|}}{N}{}^{+}-CH_2CH_2OH \quad Cl^{-} \tag{3}$$

which is an example of the widely known Menschutkin-type reaction.[4–7]   At first, we attempted the reaction by adding DMAE to the CB–BR latex, but the reaction did not proceed.   This is probably because DMAE is soluble in the water phase and the concentration of DMAE in micelles is not high enough.

We investigated the reaction at 27°C in toluene.   The result is shown in Figure 7.   The CB–BR having 0.5×10^{-4} mol/g hydroxyl and 7.1×10^{-4} mol/g chlorine was chemically modified by DMAE after 24 hr of reaction to afford the CB–BR having 3.3×10^{-4} mol/g hydroxyl.   This apparently indicates that the hydroxyl group was introduced onto 44% of the CB units.   This value is a little lower than the percent hydrolysis.

DMAE treatment was also carried out on an open-roll mill.   The results are given in Table II.   When the CB–BR having 0.6×10^{-4} mol/g hydroxyl was milled without DMAE, gelation took place during the procedure together with hydrolysis of active chlorine probably caused by adventitious moisture.   Compounded DMAE effectively prevented the polymer from gelation.   These results may be taken to indicate that DMAE reacted with unstable chlorine in CB–BR during milling to form quaternary ammonium salt attached to CB–BR.   In ad-

dition, it is also probable that DMAE acted as an acceptor of hydrogen chloride and prevented the further reaction of the acid in the rubber matrix on an open-roll mill.

References

1. S. Yamashita, K. Sando, and S. Kohjiya, *J. Appl. Polym. Sci.*, **23**, 1951 (1979).
2. D. E. Anderson and R. G. Arnord, *Ind. Eng. Chem.*, **45**, 2727 (1953).
3. S. Miura, *Kogyo Kagaku Zassi*, **64**, 405 (1960).
4. G. D. Jones, *Ind. Eng. Chem.*, **44**, 2686 (1952).
5. I. Noda and S. Kagawa, *Kogyo Kagaku Zassi*, **66**, 857 (1963).
6. G. D. Jones, W. C. Meyer, N. B. Tefertiller, and D. C. MacWilliams, *J. Polym. Sci. A-1*, **8**, 2123 (1970).
7. S. Dragon, I. Petrariu, and M. Dima, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3077 (1972).
8. S. Yamashita, S. Atomori, S. Kohjiya, and T. Miyagawa, *J. Appl. Polym. Sci.*, **17**, 3049 (1973).
9. *Dictionary of Organic Compounds*, Vol. 2, S. Nagai, Ed., Maruzen, Tokyo, 1959, p. 1140.
10. S. Yamashita, S. Kohjiya, A. Yamada, and Y. Kawakita, *Nippon Gomu Kyokaishi*, **49**, 409 (1976).
11. T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization*, Interscience, New York, 1952, p. 49.
12. A. Winston and P. Wichacheewa, *Macromolecules*, **6**, 200 (1973).
13. S. Kohjiya, Y. Imoto, and S. Yamashita, to be published.
14. G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **71**, 1396 (1949).
15. S. Kohjiya, H. Takeuchi, and S. Yamashita, to be published.
16. A. Miller, in *Organic Chemistry*, Vol. III, H. Gilman, Ed., Wiley, New York, 1953, p. 166.
17. R. D. Walker and J. E. Hawkins, *J. Am. Chem. Soc.*, **74**, 4209 (1952).
18. H. W. Melville and P. R. Sewell, *Makromol. Chem.*, **32**, 139 (1959).