1-Chlorobutadiene–Butadiene Rubber. III. Determination of Hydroxyl Group Content

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Synopsis

The hydroxyl group content in 1-chlorobutadiene–butadiene rubber prepared by emulsion polymerization (CB–BR) was determined by UV spectroscopy. CB–BR was allowed to react with phenyl isocyanate at room temperature, and the resulting N-phenyl carbamate was assayed by UV measurement. The present method allowed the determination of a very small amount of hydroxyl groups contained in a high molecular weight hydrocarbon polymer. The hydroxyl group content in the hydroxyl-terminated liquid polybutadiene was also determined. The value agreed closely with that obtained by the usual titration method. Hydroxyl groups in CB–BR are presumed to be produced by the hydrolysis of the active chlorine contained in CB–BR. This hydrolysis is dependent on the work-up conditions of CB–BR, and the quantitative results were discussed with reference to the microstructure of the 1-chlorobutadiene unit in CB–BR.

INTRODUCTION

Recently, we reported the synthesis and properties of 1-chloro-1,3-butadiene (CB) copolymer with 1,3-butadiene (Bd).[1-3] The copolymer contains carbon–carbon double bond and chlorine, and hence it is possible to be cured not only with sulfur but also with 2-mercaptoimidazoline, which is a vulcanizer for polychloroprene.[1,3] In a preceding paper,[4] it was described that an attempt at antideterioration of the copolymer was successful by using antioxidants with tertiary amino groups, which function as rubber-bound antioxidants through reaction toward chlorine bonded to the copolymer. Thus, the copolymer is a novel butadiene rubber applicable to various chemical modifications.

The object of the present study was to determine a small amount of hydroxyl groups contained in 1-chlorobutadiene–butadiene rubber obtained by emulsion polymerization (CB–BR). During the investigation of the properties of CB–BR, we sometimes observed a peak attributable to the hydroxyl group in the infrared spectra of CB–BR, especially in that of CB–BR with a higher content of CB. The CB–BR also showed the presence of oxygen by elemental analysis and gave a vulcanizate when mixed with tolylene diisocyanate on an open-roll mill and pressed at 70°C. These findings suggest the presence of hydroxyl groups in CB–BR, and the hydroxyl group is presumed to be formed by the hydrolysis of chlorine of the CB unit. Thus, our attention was called to the quantitative determination of the hydroxyl group in CB–BR and to the clarification of the influencing factors on the concentration of hydroxyl group.

Conventionally, there are several methods to determine the hydroxyl content in polymers.[5-9] However, polar solvents were employed for the titration methods,[5-7] in which high molecular weight butadiene rubber does not usually

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dissolve well. The hydroxyl contents in CB–BR were found to be too small to be determined by spectroscopic determination such as infrared[8] or proton nuclear magnetic resonance.[9] Reed et al.[10] reported a convenient method for determination of hydroxyl equivalent of poly(oxyalkylene) compounds using phenyl isocyanate. The hydroxyl group was converted to carbamate by the following reaction:

$$R—OH + Ph—NCO \rightarrow R—O—CONH—Ph$$
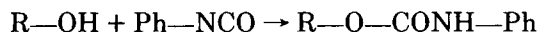
The remaining phenyl isocyanate is then back titrated by the excess of n-butylamine.[10]

Ultraviolet measurement is known to be sensitive to much smaller amounts of π-electron-containing groups than any other method. Hence, we undertook the hydroxyl group determination in CB–BR as follows: the hydroxyl group in the copolymer is treated by excess phenyl isocyanate, and the resulting phenyl carbamate group is determined by UV spectroscopy. While this study was in progress, a report was published on the hydroxyl group determination of hydroxyl-terminated low molecular weight liquid polybutadiene, using gel permeation chromatography with UV detector,[11] based on almost the same principle as ours. The purpose of the present report is to show the applicability of our method to high molecular weight polybutadiene as well as liquid polybutadiene.

EXPERIMENTAL

Materials

Hydroxyl-Terminated Polybutadiene (HT-BR)

Commercially available hydroxyl-terminated liquid polybutadiene (R-45HT; average molecular weight 2800, average functionality 2.3, hydroxyl group content 8.3×10^{-4} mole/g) was dried at 80°C under vacuum for 20 hr.

Phenyl Isocyanate (PhNCO)

Commercial PhNCO (guaranteed reagent) was distilled under reduced pressure (55–56°C/16 mm Hg) and stored under nitrogen atmosphere.

Toluene

Guaranteed reagent was washed with sulfuric acid, dried over calcium chloride overnight, refluxed over fresh calcium hydride, and distilled just before use.

Cyclohexane

Spectroscopic-grade cyclohexane was used for UV measurements.

Other Reagents

All other reagents were purified as usual or used without further purification.

Preparation of 1-Chlorobutadiene–Butadiene Copolymers

1-Chlorobutadiene–butadiene copolymers were synthesized as reported by low-temperature emulsion polymerization.[3] The polymers were reprecipitated several times (benzene–methanol) and usually dried at room temperature under vacuum.

Preparation of Phenyl Carbamates

Excess of ethyl alcohol, allyl alcohol, n-butyl alcohol, or sec-butyl alcohol was allowed to react with PhNCO at 25°C. The products were purified by repeated crystallization from petroleum ether and dried under vacuum. The analytical results, melting point, and elemental analysis coincided well with the values in the literature[12,13] and the calculated values.

Reaction Procedures with PhNCO

Rate of Reaction

Two grams CB–BR was dissolved in 70 ml toluene in a flask under agitation. Di-n-butyltin dilaurate (DBTDL, 0.0101 g) and PhNCO (0.33 ml) were then added and allowed to react at room temperature (27°C) or at 78°C under a dry nitrogen atmosphere. Two-milliliter reaction mixture samples were withdrawn with a syringe after suitable time intervals. The reaction was interrupted by adding 0.006 g of di-n-propylamine for each withdrawn sample, and the polymer was coagulated with acetone. The precipitate was washed and dried at room temperature under vacuum until a constant weight was reached, then dissolved in cyclohexane, followed by UV measurement.

OH Determination in CB–BR

About 0.15 g CB–BR was weighed, dissolved in 7 ml toluene (precipitation method) or cyclohexane (direct method), and allowed to react at room temperature (27°C) with PhNCO (0.13 ml) containing 0.0067 g DBTDL for 2 hr in a 10-ml measuring flask. After the termination of the reaction by n-propylamine (0.0097 g), toluene or cyclohexane was added until a total volume of 10 ml was reached. Thereafter, either of two methods was chosen:

1. In the precipitation method, the mixture in the flask was poured into excess acetone, and the precipitate was recovered, washed, and dried. Then, UV measurement for the precipitate was carried out, and the hydroxyl content in CB–BR was calculated as described in the following section.

2. In the direct method, phenyl-n-propylurea was separated from the mixture in the flask by centrifugation, followed by measuring the UV spectra of the solution.

OH Determination in HT-BR

The same procedures were employed for HT-BR. However, the precipitation method was not suitable because a certain amount of oligomeric HT-BR was soluble in acetone.

Analytical Measurements

UV Measurements

UV spectra were measured in cyclohexane on a Beckman DB-G grating spectrophotometer.

Elemental Analysis

Elemental analyses were performed at the Elemental Analysis Center of Kyoto University.

Determination of OH by Titration

Hydroxyl content of HT-BR was also determined by means of acetyl chloride and pyridine.[5]

RESULTS

Presence of Hydroxyl Group in CB–BR

Since CB–BR is composed of CB and Bd units, it has only carbon–carbon double bonds and chlorine as chemically functional groups. However, oxygen was detected by elemental analysis in CB–BR produced by emulsion polymerization with a higher CB fraction in the monomer feed. The results are shown in Table I. Sample 1, with a monomer feed ratio CB/Bd of 30/70, indicates the presence of oxygen, while the analytic values of the low CB-content polymers (samples 3 to 6) are nearly consistent with the calculated ones assuming the polymer is composed of CB and Bd units. The small differences between the observed and the calculated values (calculated values are shown only for sample 6) are probably due to the presence of a very small amount of hydroxyl groups (10^{-5}–10^{-4} mol/g, as shown later) and the nonrubber constituents employed in the emulsion polymerization.

The oxygen content shown in Table I was assumed to be due to the hydrolysis of active chlorine in the CB unit. In fact, the calculated values (sample 2), which are based on the assumption that the oxygen is solely derived from the hydrolysis of chlorine in the CB unit, are in fair agreement with the experimental values (sample 1). In the cases of low CB-content CB–BR, the hydroxyl group amounts were so low as not to be clearly detected by elemental analysis. If the oxygen determined by elemental analysis is due to the hydroxyl group resulting from hydrolysis of active chlorine, the hydroxyl content in CB–BR is calculated from the oxygen content. In addition, the original CB content in CB–BR should be expressed by [Cl] + [OH], because both chlorine and hydroxyl groups are derived from the CB unit only. In Table II, the results are indicated. CB–BR obtained

TABLE I
Elemental Analysis of CB–BR

Sample no.	Polymerization temperature, °C	Monomer feed (CB/Bd) weight ratio	$[\eta]$ dl/g	Elemental analysis, %				
				C	H	Cl	O	Total
1	5	30/70	—[a]	78.58	9.48	8.09	4.35	100.50
2	(Calculated)[b]		—	(78.04)	(9.52)	(8.09)	(4.35)	(100.00)
3	5	4/96	2.19	86.60	11.01	0.80	—	98.41
4	5	5/95	2.34	87.03	10.94	1.58	—	99.55
5	5	5/95	2.75	86.97	11.00	1.43	—	99.40
6	5	5/95	2.56	87.13	11.27	1.56	—	99.96
7	(Calculated)[c]		—	(87.51)	(10.97)	(1.56)	—	(100.00)

[a] Contained insoluble fraction.
[b] Calculated values assuming that Cl was attached to the CB unit and O was introduced by the hydrolysis of the Cl in the CB unit.
[c] Calculated values for the copolymer poly(CB–co–Bd) containing 1.56% chlorine.

TABLE II
Chlorine and Hydroxyl Contents in High-CB-Content CB–BR[a]

| Sample | Concentration, mol % | | |
	[Cl]	[OH][b]	[Cl] + [OH]
1	14.0	16.6	30.6

[a] CB–BR (sample 1) shown in Table I.

[b] Calculated from weight percent of oxygen by elemental analysis assuming oxygen is exclusively based on the hydroxyl group in the CB unit of CB-BR.

with high-CB feed (CB 21 mol %) contained 30 mol % CB unit. This is consistent with the monomer reactivity ratios of CB and Bd.[14]

Vulcanization of CB–BR with Diisocyanate

As mentioned above, CB-BR's were presumed to contain hydroxyl groups. These results led to the study of CB–BR on vulcanization with tolylene diisocyanate. On hundred grams CB–BR (sample 4 in Table I) was mixed with 0.14 ml tolylene diisocyanate and 30 g HAF carbon black on an open-roll mill. The compound was press cured at 70°C. The tensile properties of the vulcanizates are shown in Table III. The properties of CB–BR press cured without tolylene diisocyanate were much inferior to those in the table. These results show that the CB–BR prepared by emulsion polymerization contained hydroxyl groups to afford favorable vulcanizates upon curing with tolylene diisocyanate.

Determination of Hydroxyl Group in CB–BR

To determine the hydroxyl group in CB–BR, the polymer was treated with PhNCO, and the resulting phenyl carbamate group in the polymer was determined by UV measurement. The reaction of CB–BR with PhNCO was carried out in toluene at room temperature for 24 hr. Figure 1 shows UV spectra in cyclohexane of CB–BR (sample 4 in Table I) and CB–BR treated with PhNCO. CB–BR treated with PhNCO shows an absorption maximum at 234 nm, while the original CB–BR shows no absorption. Butadiene rubber (polybutadiene produced with organolithium compound) treated with PhNCO in the same manner did not show any absorption maximum around 234 nm. These findings suggest that the peak at 234 nm is ascribable to the $\pi \rightarrow \pi^*$ transition of the N-phenyl carbamate group introduced into CB–BR resulting from the reaction with PhNCO. Accordingly, four N-phenyl carbamates were prepared and subjected to UV measurement. The results are shown in Table IV. All the

TABLE III
Tensile Properties of CB–BR Vulcanizates[a]

	10 min[b]	40 min[b]
Modulus at 50% elongation, kg/cm²	14	17
Modulus at 100% elongation, kg/cm²	24	28
Tensile strength, kg/cm²	32	37
Elongation, %	110	105

[a] Cured with tolylene diisocyanate at 70°C; 30 phr HAF black was compounded.
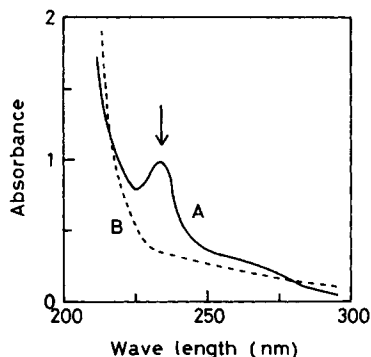
[b] Cure time.

Fig. 1. UV spectra of CB–BR and CB–BR treated with PhNCO. A, CB–BR treated with PhNCO (0.02% in cyclohexane); B, CB–BR (0.1% in cyclohexane).

carbamates showed absorption maxima in the vicinity of 235 nm. Thus, the UV absorption at 234 nm of CB–BR treated with PhNCO is attributed to the N-phenyl carbamate group introduced by the reaction of PhNCO and hydroxyl in CB–BR. As the molar absorptivity for the N-phenyl carbamate in CB–BR, we adopted 1.80 × 10⁴, and deducting the absorbance at 234 nm due to CB–BR enabled us to calculate the concentration of N-phenyl carbamate group, i.e., the hydroxyl group, in CB–BR as follows:

$$C = (E - E_0)/10\epsilon \tag{1}$$

$$C' = C/(1 - CM) \tag{2}$$

where C is the concentration of hydroxyl groups, in moles/g; E and E_0 are the absorbances when the concentrations are 1% (1 g/dl) of PhNCO-treated and untreated CB-BR's, respectively; ϵ is equal to 1.80 × 10⁴ l/mol·cm; M is the molecular weight of PhNCO; and C' is the hydroxyl content when the weight of PhNCO introduced into CB–BR is corrected. This correction does not influence the present analysis much, but if the hydroxyl content is much higher, the correction could not be neglected.

In the case of the direct method (see experimental section), several impurities may cause an error in UV measurement. The probable impurities and their UV data observed in cyclohexane solution are given in Table V. N,N'-Diphenylurea or N-propyl-N'-phenylurea were produced when PhNCO reacted with the adventitious water in the solvent or with n-propylamine added for terminating the reaction. Both ureas were almost insoluble in cyclohexane and were precipitated as they formed. They were separated adequately by centrifugation. Since DBTDL and n-propylamine had only small absorbances at 234 nm, these im-

TABLE IV
UV Spectra of Four N-Phenyl Carbamates (R—OCONH—Ph)

R	Cyclohexane[a]		Ethyl alcohol[a]	
	λ_{max}, nm	ϵ, l/mol·cm	λ_{max}, nm	ϵ, l/mol·cm
Ethyl	234	17900	237	17600
Allyl	233	17500	235	18400
n-Butyl	—	—	237	18400
sec-Butyl	234	17700	237	18000

[a] Solvent for UV measurements.

Impurity	λ_{max},[a] nm	ϵ_{234},[a] l/mol·cm
N,N'-Diphenylurea	245	null
N-Propyl-N'-phenylurea	237	null
DBTDL[b]	—	35
n-Propylamine	—	33

[a] Measured in cyclohexane.
[b] Di-n-butyltin dilaurate.

purities had only little effect on the UV data. To verify the estimate, a blank test was carried out at each determination, and the absorbance at 234 nm of the blank was deducted from that of the sample solution. Usually, the subtractions were ca. 0.01, and the observed absorbances were 0.5 to 1.5. In the precipitation method by acetone, the impurities are very soluble in the precipitant, and in this respect acetone is more preferable than methanol as precipitant.

To confirm the additivity of absorbances at 234 nm, the absorbances at 234 nm of CB–BR, ethyl N-phenyl carbamate, and their mixtures were measured. The results are given in Table VI. The additivity is recognized within experimental errors. Lambert–Beer's law was also established within the concentration range of 0.5 to 1.5 g/l (0.05% to 0.15%) concerning the CB–BR treated with PhNCO.

Reaction of Hydroxyl Group in CB–BR with PhNCO

In order to identify the concentration of phenyl carbamate groups with that of the hydroxyl groups, the reaction of PhNCO with the hydroxyl group in CB–BR should be quantitative. According to Reed,[10] PhNCO reacts quantitatively even with alcohols carrying bulky substituents.

To choose adequate reaction conditions, the influences of the reaction time and temperature were investigated for the quantitative reaction. As shown in Figure 2, the reaction rate was relatively large even at 27°C and decreased gradually to zero within 2 hr. The carbamate group in CB–BR was detected from the UV spectrum, and the result agreed well with the value obtained from the

TABLE VI
Additivity of Absorbances A at 234 nm[a]

A		Summed A values[c]	
CB–BR	Et—OCONH—Ph[b]	Calculated	Found[d]
0.093	0.584	0.677	0.681
0.093	0.412	0.505	0.507
0.093	0.290	0.383	0.388
0.093	0.209	0.302	0.303
0.093	0.107	0.200	0.218

[a] Absorbances in cyclohexane.
[b] Ethyl N-phenyl carbamate.
[c] Sum of the absorbances of CB–BR and Et—OCONH—Ph.
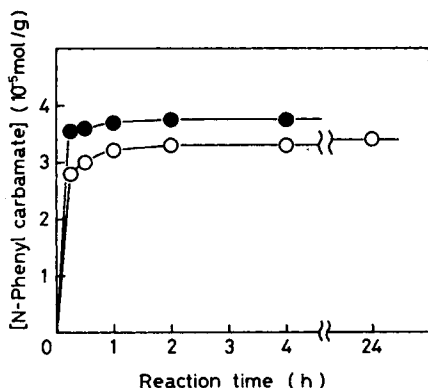[d] Found for mixtures of CB–BR and Et—OCONH—Ph.

Fig. 2. Reaction time course of PhNCO and CB–BR. Solvent toluene; CB–BR sample 6 in Table I. Reaction temperature: (O) 27°C; (●) 78°C. PhNCO concentration: (O) 1.5×10^{-3} mol/g; (●) 3.0×10^{-3} mol/g. DBTDL; 0.01 mol% PhNCO.

determination of residual PhNCO in the reaction mixture after 24 hr. At 78°C, a little (6%) higher asymptotic value for the carbamate group concentration was obtained. This can be attributed to the formation of allophanates associated with the catalytic effect of urethane groups in the reaction between isocyanates and alcohols.[15,16] For this reason, room temperature for 2 hr was preferred as the condition for the reaction of CB–BR with PhNCO.

Hydroxyl Group Contents in HT-BR and CB–BR

The results of the quantitative determinations of hydroxyl groups in HT-BR and several CB–BR's are shown in Tables VII and VIII. The results on HT-BR by the UV method (the direct method) and by the titration method, which was chosen as a standard for the present determination, coincide well with each other. This clearly indicates that the present method of determining hydroxyl groups is justifiable for polybutadienes. The precipitation method failed for HT-BR because of low molecular weight. In high molecular weight polybutadienes, the results from the direct and precipitation methods are in good agreement. Polybutadiene (BR produced with organolithium compound) and poly(CB–co–Bd) produced by solution polymerization showed no indication of the presence of hydroxyl groups (Table VII). This also seems to be reasonable.

TABLE VII
Comparison of Three Methods for OH Determination

Sample	[OH][a] by titration method (acetylation)	[OH][a] by UV method	
		Precipitation	Direct
HT-BR[b]	8.5	4.61	8.35
CB–BR[c]	—	1.68	1.72
Poly(CB–co–Bd)[d]	—	0.0	0.0

[a] Hydroxyl content, in 10^{-4} mol/g.

[b] Hydroxyl-terminated polybutadiene (R-45HT).

[c] 1-Chlorobutadiene–butadiene rubber (sample 3, see Table I and also Table VIII).

[d] Prepared in toluene by azobisisobutyronitrile at 70°C, with monomer feed of 20/80, and dried under vacuum at room temperature.

TABLE VIII
Hydroxyl Content by UV Method[a] in CB–BR Produced by Emulsion Polymerization

Sample no.	Drying condition[b]	Elemental analysis, 10^{-4} mol/g			Hydrolysis,[d] %
		[Cl]	[OH]	Total[c]	
6	A	4.4	0.3	4.7	6.4
10	A	7.1	0.6	7.7	7.8
5	B	4.0	1.4	5.4	27
3	C	2.3	1.7	4.0	43
4	C	4.5	2.9	7.4	39

[a] Precipitation method. Polymerization conditions of the samples are indicated in Table I, except for sample 10. Polymer 10 was prepared at 5°C with monomer feed ratio (CB/Bd) of 5/95, and the intrinsic viscosity was 1.08 dl/g.

[b] A: Dried under a reduced pressure at room temperature. B: Dried on an open-roll mill at 110°C for 5 min and then under reduced pressure at room temperature. C: Dried on an open-roll mill at 110°C.

[c] [Cl] + [OH].

[d] {[OH]/Total} × 100.

As shown in Table VIII, the hydroxyl content in CB–BR is much dependent upon the drying conditions. The hydroxyl group in CB–BR was estimated to be produced by the hydrolysis of chlorine in the CB unit of CB–BR. It was not directly shown that production of hydroxyl groups under these conditions is a result of hydrolysis. However, since the amounts of hydroxyl groups found in CB–BR's increased with increasing CB content and hydroxyl groups were not found in polybutadiene, their formation probably is from CB units rather than by oxidation, which would have proceeded at least as well in the butadiene units. The hydrolysis might partly occur during the emulsion polymerization, but the dependence on drying condition suggests that a larger amount of chlorine is subjected to hydrolysis after the isolation of the polymer. This is clearly seen from the data of the percent hydrolysis. Less than 10% chlorine was hydrolyzed by drying at room temperature under vacuum. Drying at elevated temperature caused more hydrolysis of the chlorine, and about 40% chlorine was converted to hydroxyl at 110°C.

DISCUSSION

In the present study, determinations of hydroxyl groups in polybutadienes were described. The spectroscopic determination of the carbamate group is applicable to very low concentrations (about 10^{-5} mol/g) on account of the large molar absorptivity (1.80×10^4). Therefore, a small amount of the hydroxyl group which reacts quantitatively with PhNCO can be determined.[10] The reaction proceeds even in nonpolar solvents such as toluene within a fairly short time; thus, the application of this method to hydrocarbon polymers is not difficult. To ascertain the reproducibility, CB–BR (sample 3) was analyzed four times. All the results fell within $(1.7 \pm 0.1) \times 10^{-4}$ mol/g. In addition, the present method is free from adventitious water. Diphenylurea, which is the reaction product of water with PhNCO, is virtually insoluble in cyclohexane and is not measured on the UV spectrometer.

There is another point of interest concerning the hydroxyl group content in CB–BR. As is noted in Table I, the oxygen content in low-CB-content CB–BR

was hardly recognized by elemental analysis, but the hydroxyl group was detected by the UV method. Poly(CB–co–Bd), which was produced by the solution polymerization in toluene, contained no hydroxyl group. These findings could be explained by assuming the presence of active chlorine in the CB copolymer. This chlorine seems to be easily hydrolyzed both during the polymerization and during the process of isolation and purification, because CB–BR was synthesized by emulsion polymerization in which water was employed as a medium.

The reactivity of chlorine is related to the microstructure of the CB unit, which is as follows:

| 1,2 | cis-1,4 | trans-1,4 | 3,4 |
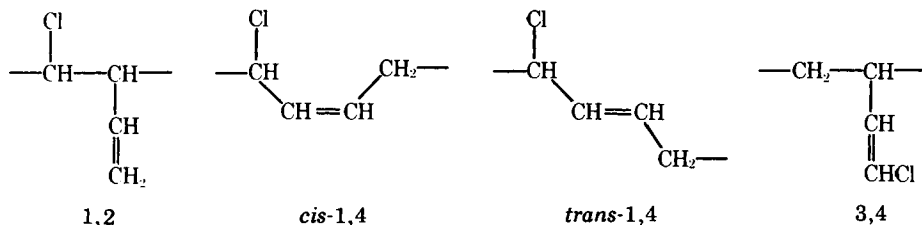
Since α,β-disubstituted ethylenes are known to be resistant to polymerization by radical initiators because of steric hindrance,[17] the 1,2-unit content would be smaller than the others. The chlorine in the 1,4-unit is much more reactive than that in the 3,4-unit, because the former is at the allylic position whereas the latter, in the 3,4-unit, is vinylic. Therefore, the chlorine in the 1,4-unit (cis and/or trans) might be subjected to hydrolysis. From Table VIII, the hydrolysis during emulsion polymerization was minor (below 10%), and in solution polymerization virtually no hydrolysis occurred, as shown in Table VII. The monomer CB, which was treated with the same procedure as the emulsion polymerization except for the absence of radical initiator, remained unchanged after the treatment. The possibility that the hydroxyl group was introduced into CB–BR by copolymerizing 1-hydroxybutadiene, which was produced from CB by hydrolysis of the chlorine, was discarded. The hydrolysis would advance more at elevated temperature. At 110°C, 40% chlorine was hydrolyzed, which could mean that at least 40% of the CB unit was in 1,4-configurations. Since the hydroxyl groups are primarily introduced during drying, it seemed difficult to control the hydroxyl content in CB–BR, but as will be shown in the next report,[18] it attains an asymptotic value by the application of heat to the latex.

References

1. S. Yamashita, S. Atomori, S. Kohjiya, and T. Miyagawa, *J. Appl. Polym. Sci.*, **17**, 3049 (1973).
2. S. Yamashita, S. Kohjiya, K. Sando, and M. Tamura, *Nippon Gomu Kyokaishi*, **49**, 162 (1976).
3. S. Yamashita, S. Kohjiya, S. Atomori, and A. Yamada, *Angew. Makromol. Chem.*, **56**, 65 (1976).
4. S. Yamashita, S. Kohjiya, and H. Nakamura, *Kobunshi Ronbunshu*, **33**, 317 (1976).
5. D. M. Smith and W. M. D. Bryant, *J. Am. Chem. Soc.*, **57**, 61 (1935).
6. G. H. Schenk, P. Wines, and C. Mojzis, *Anal. Chem.*, **36**, 914 (1964).
7. J. A. Floria, I. W. Dobratz, and J. H. McClure, *Anal. Chem.*, **36**, 2053 (1964).
8. E. A. Burns and R. F. Muraca, *Anal. Chem.*, **31** 397 (1959).
9. A. Hase and T. Hase, *Analyst*, **97**, 998 (1972).
10. D. H. Reed, F. E. Critchfield, and D. K. Elder, *Anal. Chem.*, **35**, 571 (1963).

11. J. N. Anderson, S. K. Baczek, H. E. Adams, and L. E. Vescelius, *J. Appl. Polym. Sci.*, **19**, 2255 (1975).

12. *Beilsteins Handbuch der Organischen Chemie*, 12, EIII, Bd., Springer-Verlag, Berlin, 1972, pp. 612 and 613.

13. *Beilsteins Handbuch der Organischen Chemie*, 12, EI, Bd., Deut. Chem. G., Berlin, 1929, p. 213.

14. S. Kohjiya, H. Takeuchi, and S. Yamashita, *J. Appl. Polym. Sci.*, to be published.

15. J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

16. S. L. Reegen and K. C. Frisch, *J. Polym. Sci. A-1*, *4*, 2321 (1966).

17. T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization,* Interscience, New York, 1952, p. 49.

18. S. Yamashita, K. Sando, and S. Kohjiya, *J. Appl. Polym. Sci.*, **23**, 1963 (1979).