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1-Chloro-1,3-butadiene Copolymers. III. Reactivity of 1-Chloro-1,3-butadiene in Radical Copolymerizations

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Radical copolymerizations of 1-chloro-1,3-butadiene (CB) were carried out with styrene (St), 1,3-butadiene (Bd), or chloroprene (Cp) in toluene at 70 °C by AIBN. The monomer reactivity ratios are found as follows: $r_{CB}=1.21\pm0.10$, $r_{St}=0.10\pm0.03$; $r_{CB}=0.27\pm0.02$, $r_{Bd}=0.56\pm0.03$. Copolymerization of CB and Cp showed CB was much less reactive than Cp. The Q and e values of CB were calculated to be 3.13 and +0.65, respectively. ^{1}H NMR and IR of poly(CB-co-St) showed 60% of CB units are of 1,4-configuration and the rest 3,4-configuration.

On the polymerization of 1-chloro-1,3-butadiene (CB), only a few papers[1–4] have been published up to now, while there have been so many works relevant to polychloroprene. This difference is probably due to their industrial significance. Carothers studied the polymerizations of 1,3-butadiene, chloroprene, and CB in the course of his research to synthesize a new synthetic rubber.[1] Klebanskii *et al.*[2] briefly reported the polymerizations of CB and 1-bromo-1,3-butadiene. Winston and Wichacheewa carried out the radiation-induced copolymerization of CB and styrene, and reported the monomer reactivity ratios.[3] They claimed all the CB units in the polymer are of 1,4-configuration.[3] However, in our previous studies on the polymer reactions and physical properties of CB–butadiene and CB–styrene copolymers,[4–7] it was pointed out that the CB units carried two different kinds of chlorine in their reactivity, suggesting the coexistence of two configurations of the CB unit, *i.e.*, 1,4- and 3,4-microstructures.[5–7]

In the present work, the reactivity of CB in radical polymerizations was determined relative to styrene, 1,3-butadiene or chloroprene, and the microstructure of CB units was analyzed by spectroscopic methods. This study will provide fundamental data of much importance in the syntheses and chemical modifications of CB copolymers.

Experimental

Materials. 1-Chloro-1,3-butadiene (CB) was prepared according to the method of Heasley and Lais.[8] The product was distilled twice just before use: bp 65—67 °C (lit,[8] 65—68.5 °C), yield 40%. Purity by GLPC was above 98%. Commercial 1,3-butadiene (Bd) was purified by the method previously reported.[9] Chloroprene (Cp) was distilled twice under a reduced pressure. Its purity by GLPC was 99.7%, and the trace amount of impurity (below 0.3%) was CB. Styrene (St), 2,2′-azobisisobutyronitrile (AIBN), toluene, and ethylbenzene were purified according to the usual procedures. As low mol-wt model compounds for CB units in the polymer, 1-chloro-2-butene (**1**, for the 1,4-microstructure) and 1-chloro-1-butene (**2**, for the 3,4-microstructure) were subjected to ^{1}H NMR measurements. The compound **2** was prepared by the method of Henne *et al.*,[10] and **1** was commercially available from Tokyo Kasei Kogyo Co., Ltd. Both were purified by repeated distillations.

Polymerization Procedures. Monomers, AIBN, and toluene were introduced into a glass ampoule. The ampoule was connected to a vacuum system, and was subjected to degassing, followed by the sealing *in vacuo*. When Bd was used as monomer, it was introduced into the ampoule by the vacuum distillation method. The ampoule was placed in a bath maintained at 70 °C and rotated at a speed of 24 min^{-1}. In the copolymerization of CB and Cp, the reaction was conducted under a nitrogen atmosphere and aliquots of the polymerization solution were withdrawn by a syringe at fixed time intervals. The aliquots then were mixed with acetone containing ethylbenzene as an internal standard for GLPC (carrier flow gas, hydrogen: column; LP 84, 65 °C).

Analyses of Polymers. IR and ^{1}H NMR spectra were measured on a Hitachi IR Spectrophotometer 215 and a Varian T-60A Spectrometer, respectively. Viscosity measurements were carried out in toluene using an Ubbelohde viscometer at 25.9 °C for the CB–Bd copolymer and at 30 °C for the CB–St copolymer. Copolymer compositions were determined by elemental analysis and/or ^{1}H NMR. Monomer reactivity ratios (MRRs) were calculated by the Fineman-Ross method.

Results and Discussion

Stability of CB Copolymers. The stability of poly(CB-co-Bd)s obtained by emulsion polymerization has been reported.[7] According to the results, the allylic chlorine in these CB–Bd copolymers was easily hydrolyzed to give a hydroxyl group because they were produced in an aqueous medium.[7] The CB copolymers obtained in toluene solution also contain allylic chlorines as will be described later in this paper. However, these polymers were produced under non-aqueous conditions, and could be kept unchanged for a few months. Table 1 shows the change of poly(CB-co-St) with standing time. Oxygen was detected from the CB copolymers obtained by emulsion polymeriza-

TABLE 1. ELEMENTAL ANALYSIS OF poly(CB-co-St)[a)]

Standing time[b)] d	C (%)	H (%)	Cl (%)	Total (%)
10	76.30	6.21	15.60	98.11
50	77.25	6.83	15.38	99.45
100	76.81	6.60	14.95	98.36
(Calcd)[c)]	(77.59)	(6.51)	(15.90)	(100)

a) Polymer sample No. 3 in Table 2. b) Time in day after the polymerization. c) Calculated values for poly(CB-co-St) whose CB content is 43.9 mol%.

tion,[7] but it is not the case for the poly(CB-co-St) by solution polymerization as indicated in Table 1. While the found values of C, H, and Cl contents were in good agreement with the theoretical ones even after the storage for 100 d, these polymers began to color slightly and became darker with time in several months. Therefore, all the copolymer samples were treated in a few months after the polymerization.

Copolymerization of CB with St or Bd. Elemental analysis is applicable to the composition determination of many copolymers. The compositions of CB–St and CB–Bd copolymers were determined by the elemental analysis of chlorine. In case of CB–St copolymers, their ^{1}H NMR spectra also allow us to evaluate the compositions since the phenyl protons of St units in the copolymer appear separately from the others at a lower field as shown later in Fig. 3. Table 2 shows the results of composition determination of poly(CB-co-St) both by elemental analysis and by ^{1}H NMR. A very good agreement was found between the compositions obtained by two methods. Thus, ^{1}H NMR was equally employed to determine the composition of CB–St copolymers.

The copolymer composition curves, A for poly(CB-co-St), and B for poly(CB-co-Bd), are shown in Fig. 1. The times of polymerizations were adjusted to get the conversions below 10% so that Mayo-Lewis' equation could be used to evaluate the MRRs. From the experimental points in Fig. 1, MRRs were given as follows:

Copolymerization of CB (M_1) and St (M_2),

$$r_1 = 1.21 \pm 0.10, \ r_2 = 0.10 \pm 0.03;$$

Copolymerization of CB (M_1) and Bd (M_2),

$$r_1 = 0.27 \pm 0.02, \ r_2 = 0.56 \pm 0.03.$$

The solid lines in Fig. 1 are calculated ones from these values and fit well with the experimental points. Q and e values for CB were evaluated from the MRRs with St as follows:

$$Q = 3.13, \ e = +0.65.$$

The same values from the copolymerization with Bd were $Q = 1.01$ and $e = +0.33$. These values are understandable because CB is a conjugated diene and has an electron-withdrawing chlorine. The composition curve, B, in Fig. 1 is of an inversed sigmoid shape, which suggests an alternating tendency for CB–Bd pair. Since Bd has a negative e value (-1.05[11]), the positive e value obtained for CB is in conformity with the observed alternating tendency.

Table 2. Composition determinations of poly(CB-co-St)s[a]

No.	Monomer feed (mol%) CB	St	Conversion %	CB in copolymer (mol%) ^{1}H NMR	Anal.[b]
1	100	0	17.8	100	
2	50	50	16.7	64.2	66.7
3	25	75	25.2	43.6	43.9
4	15	85	29.6	27.9	28.0
5	0	100	89.6	0	

a) [Monomer] = 4.0 M, [AIBN] = 0.02 M; temp, 70 °C; time, 86 h. (1 M = 1 mol dm^{-3}) b) From elemental analysis of chlorine.

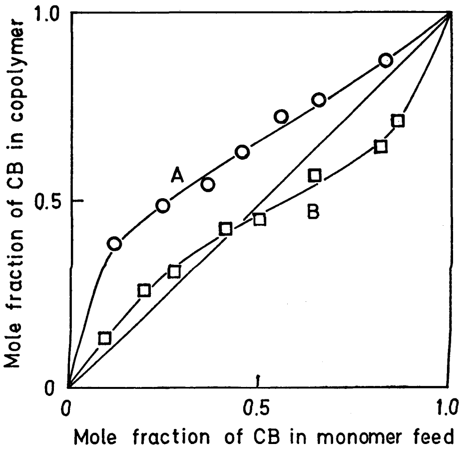


Fig. 1. Copolymer composition curves for CB–St(A) and CB–Bd(B). [Monomers] = 4.0 M, [AIBN] = 0.02 M; solvent, toluene; temp, 70 °C.

Copolymerization of CB with Cp. Both CB and Cp are diene monomers of the same molecular formula. Consequently, it was difficult to determine the composition of the copolymer accurately by elemental analysis or ^{1}H NMR. Here, in order to compare the reactivity of the two monomers, the consumptions of monomers with the time of polymerization were determined by GLPC. Figure 2 shows the amount of residual monomers plotted against time of polymerization. Curves A and B indicate the decreases of CB and Cp in their homopolymerizations, respectively, and Cp was found to be polymerized faster than CB under the present conditions. Curves C and D show the decrease of CB and Cp in their copolymerization. Again Cp was consumed faster than CB, but the difference in their consumption rates is less enhanced in the copolymerization where both polymer

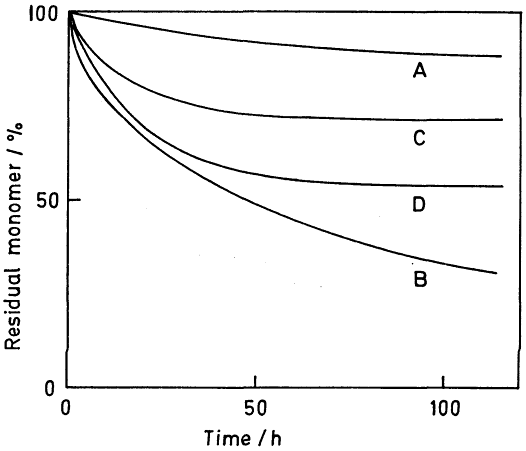


Fig. 2. Monomer consumption curves of CB(A, C) and Cp(B, D) in the homopolymerizations(A, B) and the copolymerization(C, D). Solution polymerizations in toluene at 70 °C: [AIBN] = 0.04 M. Curve A; [CB] = 5.4 M; curve B, [Cp] = 5.4 M; curves C and D, [CB] = [Cp] = 2.7 M.

radicals derived from CB and Cp are responsible for the propagation. Since the conversions from the weights of the resultant polymers agreed with those from monomer consumptions within the experimental error, it can be concluded that Cp is more reactive than CB in radical polymerization. This result is in accord with the reported difference in the reactivity between Cp and Bd ($r_{\mathrm{Cp}}=3.41$ and $r_{\mathrm{Bd}}=0.059$, or $r_{\mathrm{Cp}}=2.86$ and $r_{\mathrm{Bd}}=0.0$)[11] together with the comparable reactivity of CB with Bd described in the previous section.

Combining all the results of the polymerizations described above, we can propose the order of the monomer reactivity as follows:

$$\mathrm{Cp} > \mathrm{CB} \simeq \mathrm{Bd} > \mathrm{St}.$$

It has not been reported the successful synthesis of a new diene rubber containing chlorine by the copolymerization of Cp and Bd, probably because of the difference in their reactivities.[11] Now, CB is found to be a good candidate as a comonomer of Bd to synthesize a butadiene rubber containing chlorine. In fact, the emulsion copolymerization of CB and Bd was previously reported,[4] and the product is feasible for various chemical modifications due to allylic reactive chlorine.[6,7,12]

Intrinsic Viscosity of CB Copolymers. The three CB copolymers obtained in toluene were all soluble in toluene, and no insoluble fraction was found. In other words, the gelation did not occur in solution polymerizations, while it did occur and some insoluble parts were found in emulsion copolymerizations.[4] In Table 3 is shown the intrinsic viscosity of poly(CB-co-Bd)s prepared at various monomer feeds. The viscosities listed in Table 3 were much lower than those of the copolymers obtained by emulsion polymerization ([η]=2.5—5.5).[4] In addition, the viscosity of poly(CB-co-Bd) decreases with the increase of CB content in monomer feed. This tendency was also observed in poly(CB-co-St)s, the intrinsic viscosities of which were in the range of 0.15 to 0.30. CB monomer seems to be subject to monomer transfer reaction.

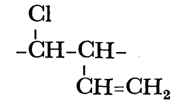
It is reasonable to get lower mol-wt copolymers by solution polymerization than by emulsion polymerization, because in the micelle the monomer can be regarded as being at the state of bulk and it is diluted in the solution. The produced polymer containing diene units is also more diluted in solution polymerization, and this fact could contribute to the absence of gelation.

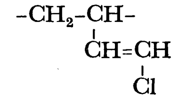
Table 3. Intrinsic viscosity of poly(CB-co-Bd)[a)]

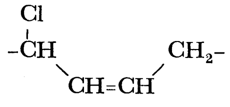
No.	CB in monomer (mol%)	Conversion %	CB in copolymer (mol%)	[η][b)] of copolymer dm^3 g^{-1}
1	0	21	0	0.163
2	20	15	25	0.111
3	40	17	42	0.109
4	65	16	57	0.081
5	85	16	70	0.069

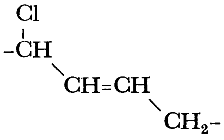
a) Polymerization conditions: [monomer]=2.5 M, [AIBN]=1.25×10^{-2} M; solvent, toluene; temp, 70 °C; time, 40 h. b) Measured in toluene at 25.9 °C.

Microstructure of CB Unit. Four kinds of microstructures are possible for CB units in the polymer:


1,2


3,4


cis-1,4


trans-1,4

In the IR spectra of poly(CB-co-St), any peak ascribable to vinyl group (*ca.* 920 cm^{-1}) was not observed. In Fig. 3, ^{1}H NMR spectra of poly(St) (A), poly(CB) (B), and poly(CB-co-St) (C) are indicated. The peak due to olefinic methylene protons in the region of *ca.* 3.8 ppm is not observed. These two experimental findings suggest the absence of 1,2-microstructure in poly(CB-co-St), and its absence confirms the reluctance of 1,2-disubstituted olefins to polymerize,[13] because CB is involved in 1,2-propagation reaction as a 1,2-disubstituted olefin. Considering the spectra of model compounds *i.e.* **1** and **2**, an assignment of the peaks in ^{1}H NMR was made as listed in Table 4. It is noticeable that the protons of CB units are

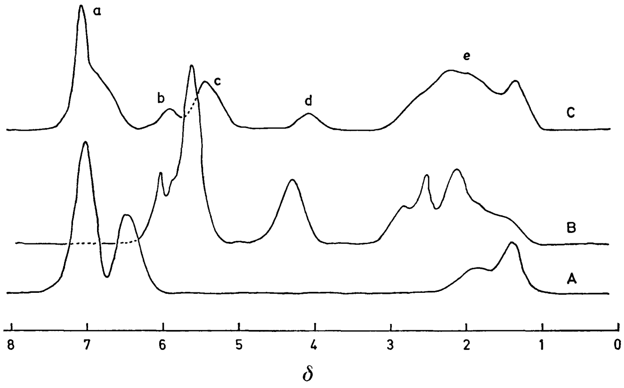


Fig. 3. ^{1}H NMR of polystyrene (A), poly(CB)(B), and poly(CB–co–St)(C) produced in toluene in the presence of AIBN.

Table 4. Assignment of ^{1}H NMR peaks in poly(CB-co-St)

Symbol	δ		Assignment
a	7.35	6.40	Phenyl proton (5H) in St
b	6.20	5.85	Olefinic proton (1H) geminal to chlorine in 3,4-CB
c	5.85	5.10	Olefinic proton in 1,4-CB (2H) and in 3,4-CB vicinal to chlorine (1H)
d	4.40	3.80	Methyne proton (1H) in 1,4-CB
e	3.20	1.10	Methyne proton in 3,4-CB (1H) and in St (1H), methylene proton in 1,4-CB (2H), in 3,4-CB (2H), and in St (2H)

subject to shielding to the higher field when CB units are incorporated in the copolymer with St. Similar shifts were observed in Bd–St and methyl methacrylate–St copolymers,[14] and this shielding effect has been interpreted in terms of the magnetic anisotropy of the phenyl group in St units. Therefore the observed shift may indicate that this poly(CB-co-St) is the true copolymer instead of the mixture of the homopolymers.

According to the assignment, the peak, a, is due to St units and the peaks, b, c, and d, are due to CB units, and the composition of poly(CB-co-St) was evaluated as shown in Table 2. Additionally, mol % of 1,4- and 3,4-microstructures could be evaluated from ^{1}H NMR, though *cis* and *trans* was not distinguishable. The results are shown in Table 5. We may conclude that in poly(CB-co-St) 60-mol% CB units are always of 1,4-configuration regardless of their contents, and the rests are of 3,4-configuration. This conclusion is in agreement with our previous estimation[5–7] from polymer reactions, while it is contrary to the result by Winston and Wichacheewa[3] who reported that all the CB units were of 1,4-configuration based on the results of the elimination reaction of hydrogen chloride from the poly(CB-co-St) obtained by the radiation-induced bulk copolymerization. Since both poly(CB-co-St)s were prepared by the radical polymerization, two copolymers have presumably almost the same microstructure. This discrepancy remains unsolved, but we suppose that their result is questionable due to the complex reactions following the hydrogen chloride elimination.

TABLE 5. MICROSTRUCTURE OF CB UNIT IN poly(CB-co-St)[a]

No.	CB in copolymer (mol%)	Microstructure[b]	
		1,4	3,4
1	100	66	34
2	87	55	45
3	77	57	43
4	73	60	40
5	64	57	43
6	54	66	34
7	52	59	41
8	39	70	30

a) Polymerization in toluene by AIBN at 70 °C. b) Mol% of CB unit in copolymer.

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