1-Chloro-1,3-butadiene Copolymers IV. Bulk Copolymerization of 1-Chloro-1,3-butadiene with Styrene

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ABSTRACT: In the bulk copolymerization of 1-chloro-1,3-butadiene (CB) and styrene (St) at 70°C, the copolymerization rate, monomer reactivity ratio (MRR), and elementary reactions governing the molecular weight of the copolymer were studied. The rate of St polymerization decreased drastically by the addition of a small amount of CB, suggesting a predominant cross-over termination, $(k_{t_{12}})$. MRRs found: $r_{CB} = 1.680$ and $r_{St} = 0.274$, hence $Q = 1.80$ and $e = 0.081$ for CB. The molecular weight of copolymer and its polydispersity decreased with an increase in CB concentration, which is interpreted by a large $k_{t_{12}}$ value. When the CB concentration becomes large, termination between CB polymer radicals may also become important.
    KEY WORDS   Copolymerization / Monomer Reactivity Ratios /
    Termination / Molecular Weight / Molecular Weight Distribution /
    1-Chloro-1,3-butadiene / Styrene /

The copolymer of 1-chloro-1,3-butadiene (CB) and 1,3-butadiene (Bd) contains active chlorines which enable it to undergo various chemical modifications.[1-3] These chlorines were estimated to be in 1,4-configurational CB units,[3] as was also the case in CB–styrene (St) copolymer.[4,5] Thus, CB copolymers are regarded as functional polymers, and their reactivities are considered interpretable from their chemical structure determined by monomer reactivity ratios (MRR), conversions, and the microstructure of CB units. Therefore, a complete characterization of the copolymer seems very important for using the CB copolymer as a functional polymer.

In a series of previous works, we attempted to characterize all aspects of poly(CB-co-St), *i.e.*, not only the overall composition but compositional distribution, monomer sequence distributions and some other molecular properties as well. In the present work, co-polymerization of CB with St in the presence of 2,2′-azobisisobutyronitrile (AIBN) was studied to elucidate the reactivity of CB in connection with the molecular weight (MW) and molecular weight distribution (MWD) of poly(CB-co-St). Polymerizations were carried out in bulk to obtain pure samples. Additionally, since only a low MW copolymer was obtained by solution polymerization,[5] bulk polymerization was preferred to solution polymerization. Monomer reactivity ratios were determined and the factors influencing the MW and MWD of the copolymer are discussed.

EXPERIMENTAL

Materials

CB was synthesized according to the method of Heasley and Lais[6]: bp 65.5—67.5°C (lit[6] 66—68°C); purity by gas-liquid chromatog-

raphy, 98.6%; IR and ^{1}H NMR spectra were fully consistent with CB. St, AIBN, and other reagents were purified by the usual methods.

Polymerization

Monomers and AIBN were introduced into a glass ampoule, which was connected to a vacuum system. The ampoule was subjected to degassing and sealed under high vacuum $(2 \times 10^{-5}$ Torr). The ampoule was placed in a bath maintained at 70°C and rotated at a speed of 24 min^{-1}. Poly(CB-*co*-St) has been reported to be relatively unstable,[5,7] probably due to HCl elimination from the backbone chain. Therefore, we used methanol containing a small amount of di-*n*-butyltin dilaurate to coagulate the copolymer. Even so, only freshly prepared copolymer was investigated.

Polymer Characterization

The number-average molecular weights of the polymers were determined by a Knauer membrane osmometer. The gel permeation chromatogram (GPC) was obtained on a Toyo Soda HLC-802UR equipped with refractive index (RI) and UV detectors: eluent, tetrahydrofuran; flow rate, 1 ml min^{-1}; column temperature, 40°C. Copolymer compositions were calculated from chlorine content determined by elemental analyses, and were in good agreement with those determined by ^{1}H NMR and thin-layer chromatography.[5,8] Monomer reactivity ratios were evaluated by the Fineman–Ross method.

## RESULTS AND DISCUSSION

Copolymerization of CB and St

Table I shows the results of the copolymerizations of CB and St made to stop at a conversion lower than 10% except No. 5. Figure 1 gives the variation in percentage conversion per minute with monomer feed composition. The percentage conversion per

Table I. Bulk copolymerization of CB and St at 70°C[a]

Sample	CB content in monomer feed mol%	Time min	Conversion %	CB content in copolymer[b] mol%
1	0	20	7.40	0
2	0.180	30	6.92	1.55
3	0.450	30	6.13	2.11
4	1.33	42	6.56	4.58
5	2.90	180	11.7	9.75
6	4.20	61	5.53	12.8
7	7.10	240	9.33	19.7
8	7.65	200	7.34	21.1
9	9.44	121	7.47	24.4
10	10.2	150	8.81	25.5
11	17.3	150	5.64	38.5
12	24.3	122	4.93	46.5
13	33.0	178	7.14	55.7
14	48.0	177	5.89	67.5
15	64.0	211	6.43	76.9
16	77.0	240	7.11	85.9
17	89.0	240	6.43	90.0
18	100	300	8.25	100

[a] [Monomer]/[AIBN] = 200.
[b] Calculated from chlorine content.
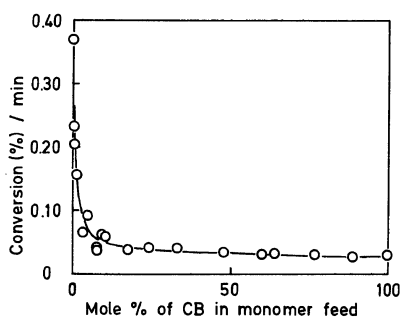
Figure 1. Rate of copolymerization of CB–St in bulk at 70°C [monomer]/[AIBN] = 200; rate is expressed by conversion(%)/min (see Table I).
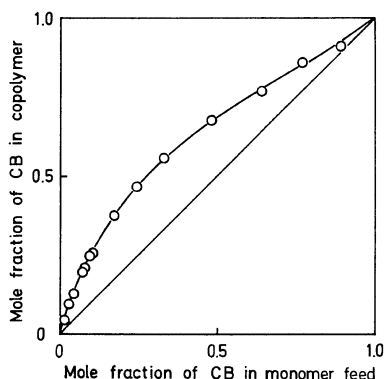
Figure 2. Copolymer composition curve of CB–St; see Table I.

minute was, exactly speaking, not a rate but a substitute for rate when [AIBN] was maintained constant and the conversions kept low. The observed drastic variation in the copolymerization rate was similar to that of St–methyl methacrylate copolymerization at 60°C by AIBN,[9] St–butyl acrylate,[10] or St–1-pyridyl-butadiene copolymerization.[11] The copolymerization rate is expressed in the form[9,12,13]

$$-\frac{d([M_1]+[M_2])}{dt} = \frac{R_i^{1/2}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)}{(\delta_1^2 r_1^2[M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2[M_1][M_2] + \delta_2^2 r_2^2[M_2]^2)^{1/2}} \quad (1)$$

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, R_i is the initiation rate, $\delta_1^2 = k_{t_1}/k_{11}^2$, $\delta_2^2 = k_{t_2}/k_{22}^2$, $\phi^2 = k_{t_{12}}^2/k_{t_1}k_{t_2}$, k_{ij} ($i, j = 1$ or 2) is the propagation rate constant for the reaction in which j-monomer adds to an i-radical, k_{t_i} ($i = 1$ or 2) is the rate constant for the mutual termination of two i-radicals, and $k_{t_{12}}$ is the crossover termination rate constant. The drastic decrease in rate of the above mentioned copolymerization systems was explained by assuming a much larger $k_{t_{12}}$ value than the k_t's of homopolymerizations, *i.e.*, ϕ to be much larger than unity.[9-11]

Figure 2 depicts the copolymer composition curve. By the Fineman–Ross method, the experimental points gave the following monomer reactivity ratios:

$$r_1 = 0.274 \pm 0.069, \qquad r_2 = 1.680 \pm 0.001$$

where M_1 and M_2 refer to St and CB, respectively. The solid line in Figure 2 is that calculated from these values. The values are somewhat different from the previous results: $r_1 = 0.10$, $r_2 = 1.21$ for the solution polymerization at 70°C by AIBN[5]; $r_1 = 0.23$, $r_2 = 1.02$ for the radiation-induced bulk polymerization.[7] To poly(CB-*co*-St) produced in bulk by AIBN at 70°C, our values are most pertinent. The Q and e values evaluated from $r_1 = 0.274$ and $r_2 = 1.680$ are:

$$Q_2 = 1.80, \qquad e_2 = +0.081$$

These are very reasonable values since CB is a conjugated monomer and chlorine is an electron-withdrawing substituent (for styrene, $Q_1 = 1.00$, $e_1 = -0.80$).[14]

From the r_1 and r_2 values, $k_{12} > k_{11}$ and $k_{22} > k_{21}$. If $k_{11} \gg k_{22}$ is the case, the order, $k_{12} > k_{11} \gg k_{22} > k_{21}$ holds and the behavior shown in Figure 1 may be explained by these differences between constants. In other words, CB is a very reactive monomer, and hence CB polymer radical is very stable. This high stability of the CB polymer radical may cause the

drastic decrease in the polymerization rate shown in Figure 1. However, the k_p value of CB (k_{22}) is not available, and it is not certain if $k_{11} \gg k_{22}$ is actually the case. A similar decrease in MW of poly(CB-*co*-St) can be better explained by the predominance of crossover termination. Therefore, the large $k_{t_{12}}$ seems a better assumption as has been estimated so far.[9-11]

Decrease in Molecular Weight of Poly(CB-co-St)

The MW of the poly(CB-*co*-St)s were measured on a membrane osmometer and the results are listed in Table II. The higher the CB content in monomer feed, the higher was the CB content in the copolymer and the smaller

the MW. We can calculate the number-average degree of polymerization from MW data, taking the copolymer composition into account. The values are shown in the last column, and decrease with CB content. The GPC measurement on poly(CB-*co*-St) indicates that the MWD is an ordinary value in radical polymerization. Since the MW of poly(CB-*co*-St) changes with CB concentration and concentration changes with conversion (see Figure 2), the MW of poly(CB-*co*-St) necessarily changes with conversion.

To ascertain the effects of CB concentration further, MW measurements on poly(CB-*co*-St)s produced at higher conversions were carried out. Table III shows the results. At these conversions, almost all CB was polymerized,

Table II. Molecular weights of poly(CB-*co*-St)s

Sample[a]	CB content in monomer feed mol%	CB content in copolymer mol%	Molecular weight[b]	Degree of polymerization[c]
1	0	0	72,300	695
2	0.180	1.55	60,000	579
3	0.450	2.11	46,700	451
4	1.33	4.58	36,100	350
6	4.20	12.76	25,700	253
8	7.65	21.43	27,700	277
9	9.44	24.43	23,300	235
11	17.3	38.49	24,400	252

[a] All samples are obtained at conversion lower than 10% (see Table I).
[b] Measured on a Knauer membrane osmometer in benzene at 37°C. The results are estimated to be with an error of about ±5.0%.
[c] Calculated from molecular weight and copolymer composition.

Table III. Molecular weights of poly(CB-*co*-St)s obtained at higher conversions

Sample	CB content in monomer feed mol%	Conversion %	CB content in copolymer mol%	Molecular weight[a]
21	2.34	80	2.95	59,900
22	3.51	75	4.70	58,700
23	4.67	70	6.60	50,700
24	5.83	70	7.84	45,100

[a] Measured on a Knauer membrane osmometer in benzene at 37°C.
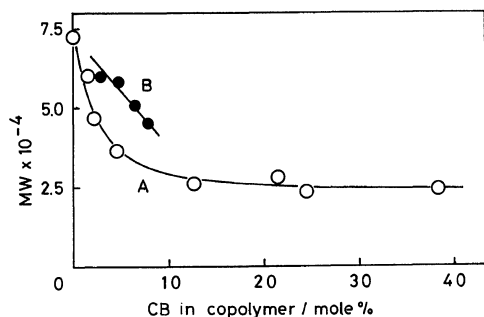
Figure 3. Number-average MW of poly(CB-*co*-St)s as a function of CB content. A, MW of the copolymers obtained at low conversions (Table II); B, MW of copolymers obtained at high conversions (Table III).

Table IV. GPC of poly(CB-*co*-St)s[a]

Sample	CB content in copolymer	MW from GPC[b]		
	mol%	M_n	M_w	M_w/M_n
31	0	24,500	43,400	1.77
32	2.85	17,300	30,500	1.76
33	5.45	15,600	26,900	1.72
34	8.83	12,300	20,300	1.66
35	18.5	11,500	17,600	1.54
36	28.5	9,000	13,800	1.53
37	43.5	8,300	12,700	1.53
38	100	6,400	9,800	1.53

[a] Synthesized by bulk polymerization at 80°C with AIBN. Conversions were between 15—20%.
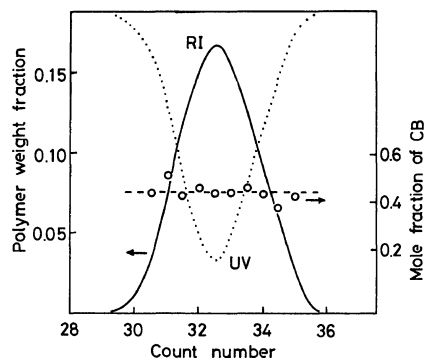[b] MW refers to that of standard polystyrenes.

and we observe the same trends in MW as in Table II. Since the decrease in CB occurs faster than that of St, the molecular weight of the copolymer should increase as polymerization proceeds. Comparison of the MW in Tables II and III is made in Figure 3 as a function of CB content in poly(CB-*co*-St). This figure clearly demonstrates the remarkable lowering of the MW of the copolymer with increase in CB content which appears to level off at higher CB content. The effect of conversion on the MW is also displayed in Figure 3. The augmentation of MW with conversion is not ascribable to the polymer reaction between the polymer radical and polymer. If this kind of polymer reaction does occur, crosslinked polymers or at least grafted polymers should be produced. However, no gel was detected in poly(CB-*co*-St)s and we did not observed any evidence suggesting the formation of grafted polymers in GPC. The number-average molecular weight of poly(CB-*co*-St) with CB content higher than 40 mol% was not available, because the polymer of lower MW than 20,000 (number average) could not be subjected to membrane osmometer measurement effective between 10^4 and 10^6. We may assume that the same trend holds for CB–St copolymers with CB content higher than that of the copolymers listed in Table II.

Figure 4. GPC of poly(CB-*co*-St), sample No. 37 (Table IV); the solid line and the dotted line are RI and UV traces, respectively, and the circles show the point-by-point compositions.

Molecular Weight Distribution by GPC

The copolymers were subjected to GPC measurements to obtain MWD data. Table IV shows the results of GPC measurements on poly(CB-*co*-St)s obtained by polymerization at 80°C. In the last column, the ratios of M_w and M_n are tabulated. With an increase in CB content in the copolymer, the ratio decreased from 1.77 for poly(St) to 1.53 for poly(CB). When CB content was higher than *ca.* 10%, the ratio appeared to reach an asymptotic value which remained constant up to the CB homopolymer.

In Figure 4, GPC curves and the point-by-point compositions of poly(CB-*co*-St) are

shown. Both RI and UV traces were unimodal; thus the ratio M_w/M_n can be an appropriate index representating the MWD of poly(CB-*co*-St). The point-by-point composition, *i.e.*, the average composition of the copolymer at each count, was calculated from RI and UV traces of GPC. This composition remained constant regardless of MW (count number). Though the copolymerization rate and MW of the copolymer depended heavily on CB concentration in the monomer feed, the invariance of that composition suggests that random copolymerization occurs between CB and St.[15,16]

Behavior of CB in Radical Copolymerization

The Q value and MRR of CB show it to be a conjugated monomer and more reactive that St. We also observed lowerings of rate (Figure 1), MW (Table II and Figure 3), and the ratio of M_w and M_n from GPC (Table IV) with increase in CB content. These lowerings were remarkably pronounced at very low CB concentrations. The rate decrease can be interpreted by the active crossover termination.

To elucidate the factors influencing the MW of poly(CB-*co*-St), a few considerations were made. As a first approximation, we assume that CB is acting as a chain-transfer agent during polymerization to determine molecular weight. In that case, the following Mayo equation should be applicable[17]:
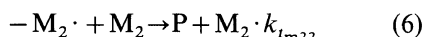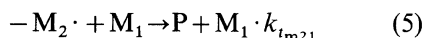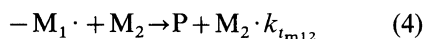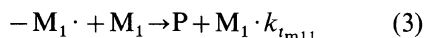
$$\frac{1}{DP} = \frac{1}{DP_0} + C_s \cdot \frac{[CB]}{[St]} \qquad (2)$$

where DP and DP_0 are the degrees of polymerization of polymers produced in the presence and absence of CB, respectively, and C_s is a chain-transfer constant. This very simple situation was not the case for the data in Table II, since the Mayo plot ($1/DP$ *vs.* [CB]/[St]) did not show any linearity.
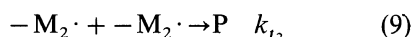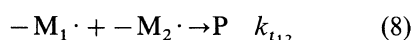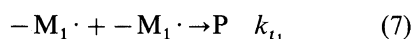
The second approach assumes a case such that both transfer to the monomer and termination are important, *i.e.*, the following reactions are considered to determine the molecular weight:

chain transfer to monomer:

$$-M_1 \cdot + M_1 \rightarrow P + M_1 \cdot k_{t_{m11}} \qquad (3)$$

$$-M_1 \cdot + M_2 \rightarrow P + M_2 \cdot k_{t_{m12}} \qquad (4)$$

$$-M_2 \cdot + M_1 \rightarrow P + M_1 \cdot k_{t_{m21}} \qquad (5)$$

$$-M_2 \cdot + M_2 \rightarrow P + M_2 \cdot k_{t_{m22}} \qquad (6)$$

termination:

$$-M_1 \cdot + -M_1 \cdot \rightarrow P \quad k_{t_1} \qquad (7)$$

$$-M_1 \cdot + -M_2 \cdot \rightarrow P \quad k_{t_{12}} \qquad (8)$$

$$-M_2 \cdot + -M_2 \cdot \rightarrow P \quad k_{t_2} \qquad (9)$$

where M_1 refers to St, M_2 to CB and P to a dead copolymer. This assumption may be reasonable, since all poly(CB-*co*-St)s were produced in bulk where no transfer reagents were present except monomers. The number-average degree of polymerization is expressed as

$$P_n = -\frac{d[M]}{dt} \bigg/ \frac{d[P]}{dt} = -\frac{d([M_1] + [M_2])}{dt} \bigg/ \frac{d[P]}{dt} \qquad (10)$$

and

$$\frac{d[P]}{dt} = R_{t_m} + \frac{1}{2} R_t \qquad (11)$$

where R_{t_m} is the rate of monomer transfer (eq 3—6) and R_t, that of termination (eq 7—9).

In radical polymerizations, monomer-transfer reactions are not considered important except for some monomers, such as allylic monomer[18] and α-methylstyrene.[19] However, a remarkable occurrence of crossover monomer-transfer reactions[12] (eq 4 and 5) seems a possible explanation for the drastic decrease in MW by CB. GPC data in Table IV, however, show this not to be the case. When the combination reaction is predominant in termination and transfer reactions are insignificant, M_w/M_n is 1.5,[20,21] and if transfers to monomer are dominating, $M_w/M_n = 2.0$.[21,22] Because M_w/M_n approached 1.5 with increase in CB

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concentration and combination was preferred to disproportionation in the copolymerization,[23] monomer–transfer reactions seem improbable. Consequently, R_{t_m} can be neglected in eq 11.

With the substitution of M_1 and M_2 by St and CB, respectively, eq 11 becomes

$$\frac{1}{\bar{P}_n} = \frac{R_i^{1/2}(r_1^2\delta_1^2[M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2] + r_2^2 \delta_2^2 [M_2]^2)^{1/2}}{2(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)} \tag{13}$$

where the stationary state is reasonably assumed, i.e.,

$$R_i = R_t$$

Equation 13 is transformed to eq 14 using $X = [M_2]/[M_1] = [CB]/[St]$.

$$\frac{1}{\bar{P}_n} = \frac{R_i^{1/2}\left(\delta_1^2 + 2\phi\frac{r_2}{r_1}\delta_1\delta_2 X + \left(\frac{r_2}{r_1}\right)^2\delta_2^2 X^2\right)^{1/2}}{2[St]\left(1 + \frac{2}{r_1}X + \frac{r_2}{r_1}X^2\right)} \tag{14}$$

The molecular weight decrease was pronounced at very low [CB], below ca. 5 mol% as seen from Figure 3 and Table II. Consequently, the second-order term of X may be neglected as a first-order approximation. Thus, eq 14 is reduced to eq 15:

$$\frac{1}{\bar{P}_n} = \frac{R_i^{1/2}\left(\delta_1^2 + 2\frac{r_2}{r_1}\frac{k_{t_{12}}}{k_{11}k_{12}}X\right)^{1/2}}{2[St]\left(1 + \frac{2}{r_1}X\right)} \tag{15}$$

$$2\frac{d[P]}{dt} = R_t$$
$$= k_{t_1}[St\cdot]^2 + k_{t_{12}}[St\cdot][CB\cdot] + k_{t_2}[CB\cdot]^2 \tag{12}$$

where St· and CB· designate the propagating radicals ending in St and CB units, respectively.

Combining eq 1, 10 and 12, we obtain

This equation is amenable to calculation, when R_i is assumed not to change between St polymerization and copolymerizations of St with CB. By that assumption, we obtain $R_i^{1/2}/2[St] = 3.92 \times 10^{-5}$. The value of r_1 and r_2 are available, and k_{11} ($= k_p$ of St) and δ_1 are found in the literature.[24] Then, eq 15 becomes eq 16:

$$\frac{1}{\bar{P}_n} = \frac{3.92 \times 10^{-5}(1350 + 4.77 \times 10^{-2}\alpha X)^{1/2}}{1 + 7.30X} \tag{16}$$

where

$$\alpha = \frac{k_{t_{12}}}{k_{22}}$$

The plot according to eq 16 ($\bar{P}_n$ vs. X) is shown in Figure 5. By computer simulation, we found the optimum value of α to be 8.0×10^6 in the range of X from 0 to 0.50. The solid line A is that calculated using $\alpha = 8.0 \times 10^6$. At a higher X region, this α value does not satisfy the experimental results. There, X^2 might not be negligible, and in that case, not eq 15 but eq 14 should be used and is converted to the following equation:

$$\frac{1}{\bar{P}_n} = \frac{3.92 \times 10^{-5}(1350 + 4.77 \times 10^{-2}\alpha X + 2.82\beta X^2)^{1/2}}{1 + 7.30X + 6.13X^2} \tag{17}$$

where $\alpha = k_{t_{12}}/k_{22}$ and $\beta = \delta_2^2 = K_{t_2}/k_{22}^2$.

By the computer simulation technique, the optimum set of α and β was found:

$$\alpha = \frac{k_{t_{12}}}{k_{22}} = 7.0 \times 10^6$$

$$\beta = \delta_2^2 = \frac{k_{t_2}}{k_{22}^2} = 50 \text{ mol s l}^{-1}$$
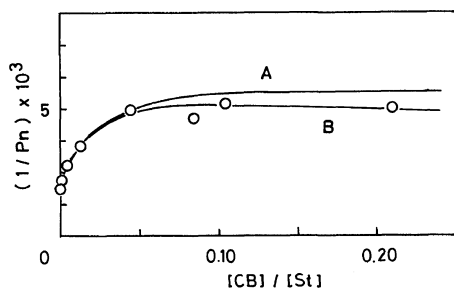
Figure 5. Relationship according to eq 16 or 17; circles are experimental points; solid line A, calculated from $\alpha = 8.0 \times 10^6$ (eq 16); solid line B, calculated from $\alpha = 7.0 \times 10^6$ and $\beta = 50 \, \mathrm{mol \, s \, l^{-1}}$.

The solid line B in Figure 5 is that calculated using these values.

As far as we know, only one report[25] treats the determination of rate constants, k_p and k_t, of 1-substituted butadiene derivatives. According to that report, these constants were not so much different from those of St as supposed by the large difference in Q values, i.e., $Q = 1.0$ (St) and $Q = 3.19$—9.57 (four 1-substituted butadienes). In the case of 1-acetoxybutadiene ($Q = 3.19$) k_t is even larger than that of St.[25] No numerical value of k_{22} is now available, but from the value, $\alpha = 7$ or 8×10^6, $k_{t_{12}}$ can be very large and, as such determines the MW of poly(CB-co-St) when $X = [CB]/[St]$ is low. At a higher CB concentration, termination between the chain ending in CB unit becomes more important. From these considerations, we estimate that the drastic decrease in rate and MW are due to the large crossover termination rate constant ($k_{t_{12}}$) between St and CB polymer radicals.

Crossover termination rate constant ($k_{t_{12}}$) has so far been discussed through:

$$\phi^2 = k_{t_{12}}^2 / k_{t_1} k_{t_2} \qquad (18)$$

This parameter is determined from the copolymerization rate (eq 1). Some established results[23] show that ϕ is equal to unity for the monomer pair where the product $r_1 \cdot r_2$ is nearly unity. The product $r_1 \cdot r_2$ is regarded as a parameter related to the alternating tendency

of a given monomer pair, i.e., the smaller $r_1 \cdot r_2$, the more alternating is the propagation. In accord with this tendency, crossover termination may be more predominant ($\phi > 1.0$) in the monomer pair when $r_1 \cdot r_2$ is smaller than unity.[12,23] In the copolymerization of St and CB, the two kinetic parameters α and β were evaluated. The parameter ϕ can be expressed by α and β as follows:

$$\phi^2 = \frac{k_{t_{12}}^2}{k_{t_1} k_{t_2}} = \frac{\alpha^2}{k_{t_1} \beta} \qquad (19)$$

Using $k_{t_1} = 8.91 \times 10^7 \, \mathrm{l \, mol^{-1} \, s^{-1}}$,[24] $\alpha = 7.0 \times 10^6$, and $\beta = 50 \, \mathrm{mol \, s \, l^{-1}}$, ϕ is calculated

$$\phi \simeq 100 \gg 1.0$$

This value should be considered only as semi-quantitative, since both α and β were obtained by the curve–fitting method on MW data. However, the large ϕ again supports the assumption that $k_{t_{12}}$ is very large for the St–CB pair.

It is noticeable that since the molecular weight of poly(CB-co-St) seems to be determined by the chemical nature of the two monomers, it depends entirely on the [CB]/[St] ratio and cannot be independent of the copolymer composition. Therefore, when we know the composition of CB–St copolymer, its molecular weight is already determined by eq 17, and because molecular weight decreases with an increase in CB content, it would be very difficult to synthesize high-CB-content poly(CB-co-St) of high molecular weight by bulk polymerization.

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