

Oxidation Behavior of Isoprene Polymers and Butadiene Polymers

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Synopsis

The oxidation behavior of *cis*-1,4-polyisoprene, emulsion polyisoprene, emulsion isoprene/styrene copolymers, and emulsion butadiene/styrene copolymers by heat aging or ultraviolet irradiation has been investigated from the change of gel fraction and molecular weight distribution. It was determined that the oxidation behavior of both isoprene and butadiene polymers is strongly dependent on the composition of the polymers as well as on the microstructure of the polymers. In the case of oxidation by heat aging, the probability ratio of chain scission to crosslinking of both isoprene and butadiene copolymers increases gradually with increasing styrene fraction. In the case of oxidation by ultraviolet irradiation, isoprene copolymers show a remarkable increase in the probability ratio of chain scission to crosslinking, whereas butadiene copolymers show substantially no change with increase in styrene fraction. It was also demonstrated that both isoprene and butadiene polymers show a greater tendency for crosslinking with oxidation by ultraviolet irradiation than with oxidation by heat aging.

INTRODUCTION

The oxidation of diene polymers has so far been investigated by a number of workers.^{1,2} It has been demonstrated that the oxidation of diene polymers in air proceeds by the mechanism of autoxidation, and both chain scission and crosslinking occur.¹

Recently, the authors³ have investigated the oxidation of emulsion isoprene/styrene copolymer (SIR) and emulsion butadiene/styrene copolymer (SBR) by heat aging or ultraviolet irradiation. It was demonstrated that SIR predominantly undergoes chain scission with oxidation by heat aging and undergoes both chain scission and crosslinking with oxidation by ultraviolet irradiation, whereas SBR predominantly undergoes crosslinking with oxidation by both heat aging and ultraviolet irradiation. It seems to be of great use from the practical point of view to clarify the difference in the oxidation behavior of isoprene polymers and butadiene polymers more precisely.

In the present paper, isoprene polymers such as *cis*-1,4-polyisoprene (CIR), emulsion polyisoprene (EIR), and SIR with two different compositions and butadiene polymers such as SBR with two different compositions were oxidized by heat aging or ultraviolet irradiation to elucidate the difference in the oxidation behavior of isoprene polymers and butadiene polymers as well as the effect of the composition of the polymers on the oxidation behavior.

TABLE I
Polymerization Recipe

Ingredient	Parts by weight
Water	200
Monomers	100
Sodium dodecylbenzene sulfonate	5.00
Cumene hydroperoxide	0.25
Iron(II)sulfate-water (1/7)	0.40
Sodium pyrophosphate	0.38
Sodium sulfate	0.50
<i>tert</i> -Dodecyl mercaptan	variable

EXPERIMENTAL

Preparation and Purification of Polymers

EIR, SIR, and SBR were prepared and purified by the following procedures. Polymerization was carried out at $10^{\circ} \pm 2^{\circ}\text{C}$ by the usual method of emulsion polymerization according to the polymerization recipe in Table I, where ingredients were purified, if necessary, by the usual method. At approximately 60% conversion, the latex was poured into an excess of isopropyl alcohol. The coagulated polymer was washed vigorously with water and methyl alcohol and dried *in vacuo* at room temperature. The polymer was purified twice by dissolving in toluene and precipitating with methyl alcohol and dried *in vacuo* at room temperature.

CIR (Kuraprene IR-10; Kuraray Co., Ltd.) was purified twice by the method described above.

Characterization of Polymers

The composition and microstructure of the polymers were determined by NMR measurement.^{3,4}

The gel fraction, intrinsic viscosity, and gel permeation chromatography (GPC) of the polymers were measured by the methods described in the previous paper.³ The molecular weight distribution and number-average molecular weight of the polymers were determined from the results of the measurement of intrinsic viscosity and GPC by the method of Kurata et al.⁵ Results of the polymer analyses are shown in Table II.

Oxidation of Polymers

Thermal aging experiments were conducted on 0.1-cm-thick films heated at 70°C in air, as has been described in the previous paper.³ Toluene solutions of the polymers (5 g/l.) were thermally aged by bubbling dry air at 70°C .

Ultraviolet irradiation experiments were conducted on 0.1-cm-thick films at 35°C in air. The irradiation source was a high-pressure mercury lamp obtained from Iwasaki Electric Co., Ltd., maintained at a distance of approximately 100 cm from the film.

TABLE II
Results of Polymer Analyses

Polymer	Composition, mole %			Gel fraction, wt %	Intrinsic viscosity, dl/g
	Isoprene	Butadiene	Styrene		
CIR ^a	100	—	—	0.0	3.85
EIR ^b	100	—	—	0.0	2.41
SIR-4	83	—	17	0.0	3.17
SIR-5	44	—	56	0.0	1.72
SBR-7	—	85	15	1.9	3.50
SRB-8	—	54	46	1.1	2.92

^a Microstructure determined by NMR measurement is as follows: *cis*-1,4 = 98.0%; *trans*-1,4 = 1.5%; 3,4 = 0.5%.

^b Microstructure determined by NMR measurement is as follows: *cis*-1,4 = 21.8%; *trans*-1,4 = 69.3%; 1,2 = 5.2%; 3,4 = 3.7%.

RESULTS AND DISCUSSION

Oxidation of Polymers by Heat Aging

In Figure 1, the change of the gel fraction of the polymers with oxidation by heat aging on films is shown. SIR-5 did not appreciably form gel with heat aging for 144 hr. It is apparent from Figure 1 that isoprene polymers exhibit a slight increase in gel fraction, whereas butadiene polymers exhibit a sharp increase in gel fraction. It is also apparent from Table II and Figure 1 that the relative rate of gel formation of both isoprene polymers and butadiene polymers is strongly dependent on the composition of the polymers as well as the microstructure of the polymers. Figure 2 shows the change of the molecular weight distribution of SIR-4 with oxidation by heat aging on films. The figure shows an increase in the low molecular weight fraction which cannot appreciably be found in the original polymer with heat aging for 96 hr. This, together with the above-described results, indicates that SIR-4 undergoes both chain scission and cross-linking with oxidation by heat aging. This was also the case for the other poly-

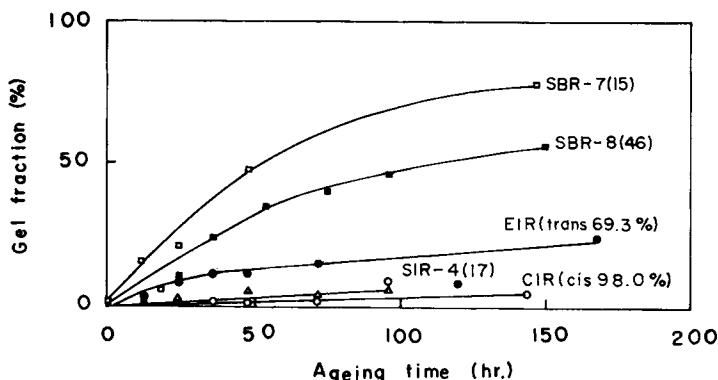


Fig. 1. Change in gel fraction of polymers with oxidation by heat aging on films: (○) CIR; (●) EIR; (△) SIR-4; (□) SBR-7; (■) SBR-8. Figures in parentheses indicate the microstructure for CIR and EIR, and the mole per cent of styrene for SIR-4, SBR-7, and SBR-8.

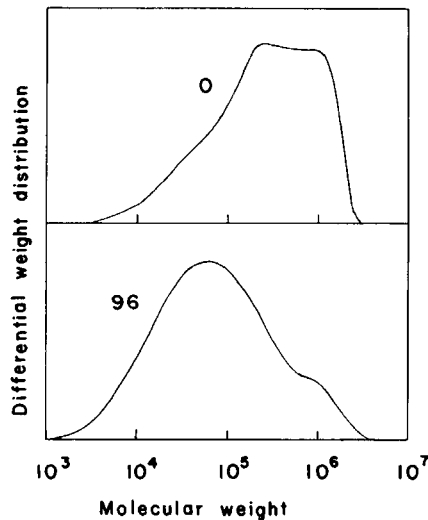


Fig. 2. Change in molecular weight distribution of SIR-4 with oxidation by heat aging on films. Figures on curves indicate the aging time in hours.

mers described in Figure 1. In this case, the probability ratio of chain scission to crosslinking can be determined from the theory of Charlesby et al.,⁶ the applicability of which has already been discussed in a previous paper.³

According to Charlesby et al.,⁶ the relationship between sol fraction s and the time of heat aging or ultraviolet irradiation, t , can be represented by the following equation:

$$s + s^{1/2} = p_0/q_0 + [1/(q_0 u_1 t)] \quad (1)$$

where p_0 and q_0 are the extents of chain scission and crosslinking, respectively, per unit time of heat aging or ultraviolet irradiation; and u_1 is the number-average molecular weight. Consequently, the probability ratio of chain scission to crosslinking, p_0/q_0 , can be determined as the intercept of the plot of $s + s^{1/2}$ against $1/t$. The values of p_0/q_0 thus obtained for oxidation by heat aging on films are shown in Table III. The values of p_0/q_0 for SIR-4 and SBR-7 in this table are almost consistent with those for SIR and SBR, respectively, reported in the previous paper.³

The relationship between the oxidation behavior and composition of the emulsion polymers is demonstrated in Figure 3. It is apparent from this figure

TABLE III
Oxidation Behavior of Polymers by Heat Aging on Films

Polymer	Probability ratio of chain scission to crosslinking ^a
CIR	1.95
EIR	1.62
SIR-4	1.93
SBR-7	0.43
SBR-8	0.93

^a p_0/q_0 in eq. (1).

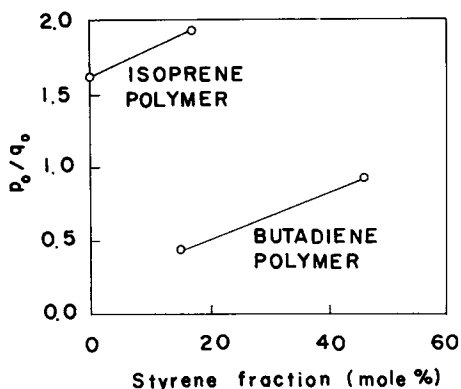


Fig. 3. Relationship between probability ratio of chain scission to crosslinking and composition of the emulsion polymers for oxidation by heat aging on films: p_0/q_0 = probability ratio of chain scission to crosslinking.

that both isoprene polymers and butadiene polymers show an increase in p_0/q_0 with increase in styrene fraction, which may predominantly be attributed to the decrease in q_0 with decrease in diene fraction. It is also apparent from Figure 3 that isoprene polymers show larger p_0/q_0 ratios than butadiene polymers. This may reflect the substantial difference in the chemical reactivity of isoprene polymers and butadiene polymers.^{7,8} The difference in p_0/q_0 of CIR and EIR in Table III may be attributed to the difference in the microstructure of the polymers described in Table II.

In Table IV is shown the change in intrinsic viscosity or number-average molecular weight of isoprene polymers with oxidation by heat aging in solution.

TABLE IV
Change of Intrinsic Viscosity or Number-Average Molecular Weight of Isoprene Polymers with Oxidation by Heat Aging in Solution

Polymer	Aging time, hr	Intrinsic viscosity, dl/g	Number-average molecular weight $\times 10^{-5}$
CIR	0	3.85	2.81
	6	2.85	1.81
	12	2.15	1.45
	36	1.01	0.84
	48	0.74	0.65
	72	0.53	0.47
	100	0.39	0.35
EIR	0	2.41	—
	6	1.87	0.65
	12	1.58	0.53
	24	1.10	0.50
	48	0.71	0.37
SIR-4	0	3.17	—
	6	2.71	0.96
	12	2.40	0.92
	24	2.11	0.84
	72	1.55	0.74
	96	1.44	0.69

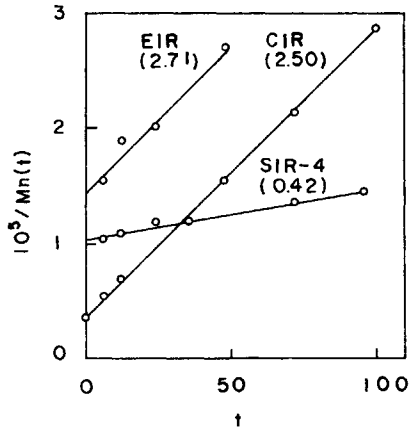


Fig. 4. Relationship between reciprocal of number-average molecular weight and time of heat aging: $M_n(t)$ = number-average molecular weight at time t ; t = time of heat aging in hours. Figures in parentheses indicate the values of $k \times 10^7$ in eq. (2).

The polymers in Table IV did not form gels, with heat aging for about 100 hr. It is apparent from Table IV that the polymers exhibit a sharp decrease in number-average molecular weight, which means that the polymers predominantly undergo chain scission, because it is believed that the polymers do not appreciably undergo crosslinking in such dilute solutions.⁹ In this case, the relationship between the rate of chain scission, k , and number-average molecular weight of the polymers can be described by the following equation^{9,10} on the assumption that the rate of chain scission is independent of the time of heat aging:

$$1/M_n(t) = 1/M_n(0) + kt \quad (2)$$

where t is the time of heat aging, $M_n(0)$ is the number-average molecular weight of the polymers at time zero, and $M_n(t)$ is the number-average molecular weight

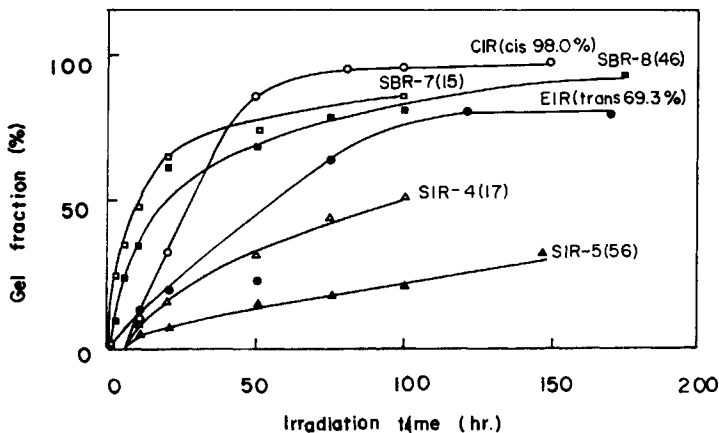


Fig. 5. Change in gel fraction of polymers with oxidation by ultraviolet irradiation on films: (O) CIR; (●) EIR; (△) SIR-4; (▲) SIR-5; (□) SBR-7; (■) SBR-8. Figures in parentheses indicate the microstructure for CIR and EIR, and the mole per cent of styrene for SIR-4, SIR-5, SBR-7, and SBR-8.

TABLE V
Oxidation Behavior of Polymers by Ultraviolet Irradiation on Films

Polymer	Probability ratio of chain scission to crosslinking ^a
CIR	0.07
EIR	0.41
SIR-4	0.88
SIR-5	1.31
SBR-7	0.30
SBR-8	0.22

^a p_0/q_0 in eq. (1).

of the polymers at time t . Consequently, the rate of chain scission k can be determined as the slope of the plot of $1/M_n(t)$ against t .

Figure 4 shows the relationship between $1/M_n(t)$ and t . It is apparent that the points in Figure 4 fit straight lines, as expected from eq. (2). The values of k thus obtained for oxidation by heat aging in solution are also shown in Figure 4. It is apparent from Figure 4 that the rate of chain scission of CIR is not so much different from that of EIR, which indicates that the difference in the microstructure of the polymers described in Table II has little effect on the rate of chain scission. On the contrary, it is also apparent from Figure 4 that the rate of chain scission of SIR-4 is much smaller than that of EIR. This may partly be explained by the difference in the composition of the polymers. It seems, however, that the above-described oxidation behavior by heat aging in solution cannot directly be correlated to that by heat aging on films. Further investigations seem to be necessary to settle this difficulty.

Oxidation of Polymers by Ultraviolet Irradiation

Figure 5 shows the change of the gel fraction of the polymers with oxidation by ultraviolet irradiation on films. It is apparent from Table II and Figure 5 that,

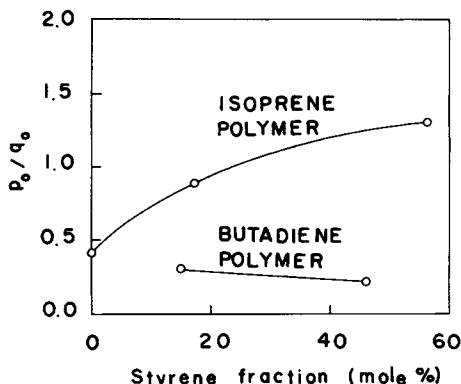


Fig. 6. Relationship between probability ratio of chain scission to crosslinking and composition of the emulsion polymers for oxidation by ultraviolet irradiation on films: p_0/q_0 = probability ratio of chain scission to crosslinking.

although both isoprene polymers and butadiene polymers exhibit a substantial increase in gel fraction, the relative rate of gel formation of both polymers is strongly dependent on the composition of the polymers as well as the microstructure of the polymers. Also in this case, it was confirmed from the change of the molecular weight distribution of the polymers that the polymers in Figure 5 undergo both chain scission and crosslinking on oxidation by ultraviolet irradiation. Consequently, it is possible to determine the probability ratio of chain scission to crosslinking, p_0/q_0 , as has been described in the previous section.

Table V shows the values of p_0/q_0 for oxidation by ultraviolet irradiation on films. The values of p_0/q_0 for SIR-4 and SBR-7 in Table V are almost consistent with those for SIR and SBR, respectively, reported in the previous paper.³ The relationship between the oxidation behavior and composition of the emulsion polymers is demonstrated in Figure 6. It is apparent from this figure that isoprene polymers show a remarkable increase in p_0/q_0 with increase in styrene fraction, which may be attributed to the decrease in q_0 with decrease in diene fraction. It is also apparent from Figure 6 that, in the styrene fraction range of about 15–45 mole %, isoprene polymers undergo both chain scission and crosslinking, whereas butadiene polymers predominantly undergo crosslinking. Such a remarkable difference in oxidation behavior may represent the substantial difference in the chemical reactivity of isoprene polymers and butadiene polymers.^{7,8} The difference in p_0/q_0 of CIR and EIR in Table V may be attributed to the difference in the microstructure of the polymers described in Table II.

Compared with the oxidation behavior by heat aging on films described in the previous section, it is clear that both isoprene polymers and butadiene polymers, especially isoprene polymers, show a greater tendency to crosslink formation with oxidation by ultraviolet irradiation than with oxidation by heat aging. This is consistent with the conclusion in the previous paper.³

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References

1. W. O. Lundberg, *Autoxidation and Antioxidants*, Interscience, New York, 1962, pp. 857–918.
2. P. M. Norling, T. C. P. Lee, and A. V. Tobolsky, *Rubber Chem. Technol.*, **38**, 1198 (1965).
3. K. Sakota, K. Okuno, T. Okaya, and S. Tsuchiya, *J. Appl. Polym. Sci.*, **20**, 2811 (1976).
4. Y. Tanaka, Y. Takeuchi, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci. A-2*, **9**, 43 (1971).
5. M. Kurata, H. Okamoto, M. Iwama, M. Abe, and T. Homma, *Polym. J.*, **3**, 739 (1972).
6. A. Charlesby and S. H. Pinner, *Proc. Roy. Soc. A*, **249**, 367 (1959).
7. J. O. Cole and J. E. Field, *Ind. Eng. Chem.*, **39**, 174 (1947).
8. J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).
9. C. E. Herrick, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1849 (1974).
10. R. T. Conley, *Thermal Stability of Polymers*, Marcel Dekker, New York, 1970, pp. 91–94.

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