Acetylene–Butadiene Copolymer for Polymer Coatings

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Synopsis

Low molecular weight, $\bar{M}_n$ 1800–2400, and soluble copolymers of acetylene and butadiene were prepared by nickel naphthenate–diethylaluminum chloride catalyst. These copolymers possess high cure tendency to give insoluble and highly crosslinked films. The curing ability can be controlled by the amount of acetylene content in the copolymer and is in the following order: acetylene–butadiene copolymer > tung oil > *cis*-1,4-polybutadiene ≫ linseed oil, 1,2-polybutadiene, butadiene–isobutylene copolymer. Chemical modifications of the copolymer such as maleic reaction, metallation by lithium or sodium, graft polymerization by methyl methacrylate, 4-vinylpyridine or vinyl acetate, and epoxidation were also examined. The divinyl methylene in the copolymer gives a high cure tendency and high chemical reactivity.

INTRODUCTION

Low molecular weight polymers or copolymers of various kinds of diolefin, such as butadiene, isoprene, chloroprene, or dicyclopentadiene have been recently industrialized for drying oil or paint raw material.[1-3] They have excellent properties as coating material, but in general the drying rate seems too slow as compared with natural drying oils. The authors have described a copolymer of acetylene and butadiene[4-6] which possesses an active methylene group neighboring two double bonds and is expected to have high reactivity towards oxygen and other reagents.

This report deals with drying properties of the copolymer and its derivatives modified by the reaction with maleic anhydride, vinyl monomers, metallation, or epoxidation.

EXPERIMENTAL

The copolymer was prepared by the method previously mentioned.[4] Copolymers were stored without a stabilizer in a nitrogen atmosphere. The antioxidant was not added in the course of the copolymerization's termination. The ash content in copolymers was less than 10^{-2} wt %.

Cure of Copolymers by Oxygen

The curing tendency of the copolymers was examined as follows: A glass slide (76 × 26 mm) was coated with the copolymer with or without the drier at a

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thickness of about 30 μ and then was exposed to air at a given temperature and in a given time. After the cure, the copolymer-coated glass plate was dipped into toluene and extracted overnight at room temperature, and then dried *in vacuo.* The weight ratio of toluene-insoluble parts to initially mounted copolymer was taken as a measure of cure. A delamination of highly crosslinked films was negligibly small and did not give misleading results.

Chemical Modification of Copolymers by Unsaturated Compounds

Maleic anhydride-modified copolymers were prepared as follows: Copolymers, maleic anhydride, and benzoyl peroxide were dissolved in toluene in a glass flask and heated for 4 hr at 90°C with agitation. After the reaction, the toluene solution was evaporated to about $\frac{1}{4}$ of the volume *in vacuo* at room temperature, and then poured into a large excess of methanol. The precipitated polymer thus obtained was dried *in vacuo.* The content of maleic anhydride of the products was measured by Fritz's method,[7] dissolving the sample into benzene, adding $\frac{1}{3}$ volume of methanol, and titrating with $0.1N$ sodium methoxide solution of benzene–methanol (3:1 volume ratio) using thymol blue as an indicator.

The reaction of copolymers and vinyl monomers was carried out as follows: The copolymer and vinylpyridine or vinyl acetate and a radical initiator were dissolved in toluene. The reaction was carried out at the refluxing temperature of the solution. After the reaction, toluene was evaporated and the recovered product was washed with methanol repeatedly.

Metallation of Copolymers and Related Reactions

Metallation of copolymers was carried out in a nitrogen atmosphere with electromagnetic stirring. Fine chips of lithium metal or sodium metal were added to a copolymer solution. The amount of metal–carbon bond was determined using allyl bromide by the double titration method according to Gilman et al.[8]

The carboxylation reaction of lithiated copolymers was performed by pouring the metalated copolymer into a slurry of Dry ice–tetrahydrofuran. The mixture was acidified with oxalic acid and then poured into a large amount of methanol to precipitate the carboxylated copolymer. After the polymer was dried *in vacuo,* the carboxyl group content was determined by titrating with $0.1N$ alcoholic potassium hydroxide solution in pyridine using phenolphthalein as an indicator.

Epoxidation of Copolymers

The copolymer, dichloroethane solvent, acetic acid, and an ion exchange resin (Amberlite IR 120 converted to —SO_3H type) were charged into a glass flask. Aqueous solution of hydrogen peroxide (30%) was added at room temperature with agitation. Then, the reaction temperature was raised to 60°C and maintained at the same temperature for 2 hr. At the end of this time, twice the volume of water was added into the reaction mixture. After the separation of the aqueous layer and the ion exchange resin, the dichloroethane solution was washed with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate, and then evaporated. The epoxy content of the polymers was determined by King's method,[9] adding $0.2N$ HCl dioxane solution and titrating with

0.1N NaOH solution using cresol red as indicator. Durbetaki's method[10] using HBr–acetic acid was not suitable, because HBr reacted with the copolymer to form a gel.

RESULTS AND DISCUSSION

The viscous liquid copolymers are prepared by the method previously mentioned.[4] The intrinsic viscosity and molecular weight of copolymers were found to be about 0.08–0.13 dl/g at 30°C in toluene and $\bar{M}_n$ 1800–2400 using a Hitachi Perkin–Elmer 115 vapor pressure osmometer. The copolymers are soluble in dichloromethane, chloroform, carbon tetrachloride, dichloroethane, hexane, cyclohexane, benzene, toluene, xylene, ethylbenzene, tetrahydrofuran, diethyl ether, dioxane, dimethoxyethane, carbon disulfide, and ethyl acetate, and partly soluble in acetone, methyl ethyl ketone, and dimethylformamide. However, the copolymers are insoluble in methanol and ethanol. The copolymers have a good storage stability at a cool place for several months without a stabilizer. The addition of a stabilizer extends the storage stability, and the amount of a stabilizer added will prolong drying time. The compatibility of copolymers with linseed oil, tung oil, and other synthetic drying oils or pigments is fairly good. Faint yellowish copolymers become reddish with increase in the acetylene content of copolymers. Copolymers containing acetylene unit from 5 to 50 mole % are obtained. The color of the copolymers gradually declines with extending the cure and the copolymers become almost colorless and transparent having a glossy surface at full hardness.

Cure of Copolymers by Oxygen

Synthetic drying oils and natural drying oils react gradually with oxygen on exposure to air. In the absence of curing catalyst, several weeks are required

TABLE I
Hardening of the Polymer on Exposure to Air at 30°C

Sample	Exposure time, days	(Toluene-insoluble/ initial polymer) × 100, wt %
Acetylene–butadiene copolymer[a]	1	90
	2	100
	3	102
	4	109
Acetylene–butadiene copolymer[b]	3	74
	5	103
	10	118
	13	110
Tung oil	2	11
	5	60
	12	101
	14	105
Linseed oil	7	0
	14	1
	17	10
	20	24

[a] Acetylene content, 31.8 mole %; $\bar{M}_n$, 2370.

[b] Acetylene content, 22.6 mole %.

TABLE II
Hardening of the Polymer on Exposure to Air at 100°C

Sample	Exposure. time, min	(Toluene-insoluble/ initial polymer) × 100, wt %
Acetylene–butadiene copolymer[a]	20	80
	30	118
	40	107
Acetylene–butadiene copolymer[b]	30	81
	40	107
	50	130
Acetylene–butadiene copolymer[c]	20	76
	30	85
	40	85
Tung oil	45	83
	70	85
	90	88
Linseed oil	60	0
	120	0
	240	0
cis-1,4-Polybutadiene[d]	20	4
	30	12
	40	48
	60	89
cis-1,4-Polybutadiene[e]	30	0
	40	0
	60	7
1,2-Polybutadiene[f]	60	0
	120	0
	240	0
Butadiene–isobutylene copolymer[g]	60	0
	120	0
	240	0

[a] Acetylene content, 31.8 mole %; $\overline{M}_n$, 2370.
[b] Acetylene content, 23.7 mole %.
[c] Acetylene content, 10.3 mole %.
[d] Polyoil Hüls 110, $\overline{M}_n$, 1400.
[e] Polyoil Hüls 130, $\overline{M}_n$, 3200.
[f] Nippon Soda B 1000; $\overline{M}_n$, 1130; 1,2-, 91.2%; trans, 8.8%; cis, 0%.
[g] Tōnen Sekiyu Kagaku SK 1000; $\overline{M}_n$, 550; iodine index, 190.

for crosslink formation, depending on the kind of drying oils. Table I illustrates the data of hardening at 30°C without curing catalyst. The acetylene–butadiene copolymer containing 31.8 mole % of acetylene becomes completely insoluble within one to two days, whereas the copolymer containing 22.6 mole % of acetylene dries within four to five days. On the other hand, tung oil, which is the most active natural drying oil, needs 12 days to cure. Linseed oil does not dry even in 20 days. This indicates that the copolymers possess high hardening ability which is controlled by the amount of acetylene content in the copolymers.

Tables II and III summarize the cure data of polymers at elevated temperatures as 100°C and 250°C without drying catalyst. Linseed oil, 1,2-polybutadiene, and butadiene–isobutylene copolymer do not show air drying within 240 min at 100°C, whereas acetylene–butadiene copolymers dry from several to ten minutes. The cure data indicate the following drying activity: acetylene–

TABLE III
Hardening of the Copolymer on Exposure to Air at 250°C

Sample	Exposure time, min	(Toluene-insoluble/ initial polymer) $\times$ 100, wt %
Acetylene–butadiene copolymer[a]	10	100
	20	100
	30	110

[a] Acetylene content, 31.8 mole %; $\overline{M}_n$, 2370.

butadiene copolymers > tung oil > cis1,4-polybutadiene >> linseed oil, 1,2-polybutadiene, butadiene–isobutylene copolymer. The drying activity of the copolymers can be changed by changing the acetylene content in the copolymers. The cured copolymers of acetylene and butadiene are almost colorless having glossy surfaces without alligatoring and crimping. However, the copolymers cured at 250°C have a somewhat brownish color, whereas the drying time is as short as 10 min, indicating possibly the special utility of the copolymers as a matter for a coating of steel at hot state.

Generally, the drying rate of polymers can be accelerated by the addition of a conventional drying catalyst such as cobalt, manganese, ferrous, calcium, zinc, or lead compound. According to preliminary experiments, it was found that the cobalt compound is the best drying catalyst, because the catalytic activity

TABLE IV
Hardening of the Polymer in the Presence of Cobalt Naphthenate Drier
on Exposure to Air at Room Temperature[a]

Sample	Exposure time, days	(Toluene-insoluble/ initial polymer) $\times$ 100, wt %
Acetylene–butadiene copolymer[b]	1	106
	2	115
Tung oil	1	55
	2	80
	3	92
	12	100
Linseed oil	1	25
	3	51
	7	76
	12	77
1,2-Polybutadiene[c]	1	0
	3	43
	6	91
	8	112
Butadiene–isobutylene copolymer[d]	2	1
	4	2
	7	3
	12	3

[a] Cobalt metal added, 0.1 parts with respect to 100 parts polymer.
[b] Acetylene content, 31.8 mole %; $\overline{M}_n$, 2370.
[c] Nippon Soda B 1000; $\overline{M}_n$, 1130.
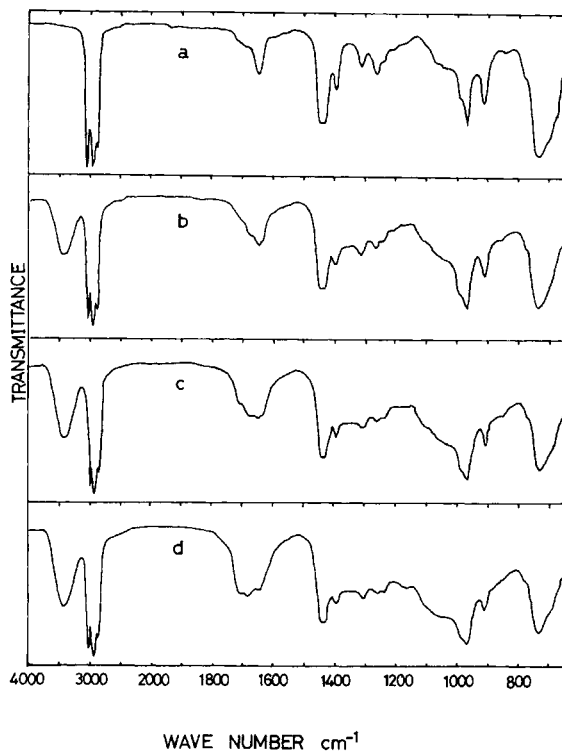[d] Tōnen Sekiyu Kagaku SK 1000, $\overline{M}_n$, 550.

Fig. 1. Change of IR spectra of copolymer cured by oxygen at room temperature: (a) initial; (b) after two days; (c) after three days; (d) after 20 days.

of cobalt compound is very high compared with other driers. However, the amount of cobalt compound added to the copolymer of acetylene and butadiene had better be limited to less than that noted in Table IV. The addition of a large amount of cobalt compound retards the formation of the glossy surface by crimping at full hardness.

The cure data using the cobalt drier are listed in Table IV. The acetylene–butadiene copolymer is cured within one day to full hardness. It is noteworthy that the time for becoming finger-dry for the copolymer of acetylene and butadiene is only several minutes under the conditions described, while other polymers need several days. Consequently, 0.01–0.05 wt % of cobalt drier with respect to the acetylene–butadiene copolymer may preferably be used for practical purposes.

The full-cured copolymers of acetylene and butadiene on the glass plate form glossy films sticking to the glass plate. At full hardness, the weight of copolymers increases by up to 10–30 wt % with respect to the amount of initial copolymers. The weight gain may be related to the amount of oxygen reacted with the copolymers. For instance, the oxygen content determined from oxygen analysis of thoroughly dried and then delaminated film containing 31.8 mole % acetylene unit was 27.1 wt %, while the weight gain was ca. 30 wt %.

The infrared spectra of copolymer containing 31.8 mole % acetylene in the course of oxygen cure without a cure catalyst are shown in Figure 1. The spectra of the copolymer coated on KBr plate were recorded on a Hitachi EP-I_2 pho-

TABLE V
Addition Reaction of Maleic Anhydride at 90°C for 4 hr[a]

Sample	Maleic anhydride, g	Benzoyl peroxide, g	Added maleic anhydride to polymer,[b] g
Acetylene–butadiene	0.65	0.156	0.32
copolymer[c]	0.65	0	0.04
	4.90	0	0.20
1,2-Polybutadiene[d]	4.90	0	0.00
cis-1,4-Polybutadiene[e]	4.90	0	0.00

[a] Initial sample polymer, 2.37 g; solvent, 100 ml toluene.
[b] Determined by Fritz's method.
[c] Acetylene content 24.0 mole %, $\bar{M}_n$, 2360.
[d] Nippon Soda B 1000, $\bar{M}_n$, 1130.
[e] Cis 81.2 %, trans 15.9 %, 1,2-, 2.9 %, $\bar{M}_n$, 1990.

tometer. On curing, the absorption at 735 cm^{-1} became weaker than those at 970 and 910 cm^{-1}, indicating that the cis double bond seems to be consumed more rapidly than the trans and vinyl double bond. The absorption bands at 1730–1600 cm^{-1} and ca. 3450 cm^{-1} became stronger with increasing the air exposure time. The former absorptions are due to a carbonyl-containing structure and the latter, to a hydroxyl group. The broad adsorptions at 1150–1060 cm^{-1} may be due to an ether linkage. The formation of peroxide, hydroperoxide, and epoxide is not confirmed by the infrared analysis.

Polymer radicals initiate a graft polymerization of vinyl monomers. For instance, the mixture of 2 g acetylene–butadiene copolymer (acetylene content 22.5 mole %, $\bar{M}_n$ 2360), 28 g methyl methacrylate, and 0.002 g cobalt naphthenate (calculated as metal) was stored for 24 hr in an atmosphere of air. The product mass was substantially insoluble in many organic solvents, showing the complete graft polymerization of methyl methacrylate. A similar result is also obtained in the system of styrene comonomer.

Chemical Modification of Copolymers by Unsaturated Compounds

Drying oils are often modified by a reaction with unsaturated compounds to form an adduct or a copolymerized oil like maleic oil[11] or styrenated oil.[12]

TABLE VI
Monomer Addition to the Copolymer at Reflux Temperature for 24 hr[a]

Monomer	Toluene, ml	Radical catalyst, g	Yield, g
4-Vinylpyridine	50	0	2.17
4-Vinylpyridine	50	benzoyl peroxide (0.059)	2.24
4-Vinylpyridine	50	azobisiso-butyronitrile (0.040)	2.24
Vinyl acetate	30	0	2.07

[a] Monomer, 2.00 g; acetylene–butadiene copolymer, 2.00 g; acetylene content, 31.8 mole-%; $\bar{M}_n$, 2370.

Usually, the preparation of maleic oils was done at about 200°C. Table V shows the reaction of maleic anhydride and copolymer or polybutadiene. The reaction temperature was lower than that of the conventional maleic reaction. Since the copolymer is very reactive toward maleic anhydride, the reaction can be performed under mild conditions. During the reaction, neither gelation nor isomerization of the carbon–carbon double bond to form conjugation were observed. The latter was confirmed by the IR and NMR spectra.

Table VI illustrates the reaction of copolymer with 4-vinylpyridine or vinyl acetate. The yield is calculated based on the methanol-insoluble part, indicating that the isolated polymers do not include homopolymer of vinylpyridine or vinyl acetate and are thought to be graft polymers. The products were completely soluble in many organic solvents.

Metallation of Copolymers and Related Reactions

The acetylene–butadiene copolymers possess many divinyl methylenes and may be more readily metallated with alkali metal than polybutadiene.[13] In fact, the copolymer was easily metallated even by lithium metal as shown in Table VII. On the other hand, cis-1,4-polybutadiene having $\bar{M}_n$ 1990 and 81.2% cis-1,4-, 15.9% trans-1,4-, and 2.9% 1,2-linkage was not lithiated under the reaction conditions described in Table VII. The copolymer solution was at first yellow and clear and then changed to black and opaque as lithiation proceeded, indicating a high degree of lithiation. The metallation using metal sodium is also possible.

The metallated copolymer can be modified by the reaction with various chemical reagents. Table VIII summarizes the result of carboxylation of copolymer and polybutadiene. The copolymer was readily carboxylated, while cis-1,4-polybutadiene was not carboxylated under the same reaction conditions.

The metallated copolymer also initiates anionic graft polymerization of styrene, isoprene, etc. The color of the polymerization system was initially black

TABLE VII
Metallation of the Copolymer with Lithium or Sodium Metal

Acetylene–butadiene copolymer (acetylene content, 24.0 mole %; $\bar{M}_n$, 2360)	1.21 g
Dimethoxyethane	50.8 ml
Lithium metal	0.88 g
Reaction temperature	82°C
Reaction time	24 hr
Metallated monomer unit[a]	9.8 mole %
Metallated divinyl methylene unit[b]	24.7 mole %
Acetylene–butadiene copolymer (acetylene content, 16.3 mole-%; $\bar{M}_n$, 1970)	2.00 g
Tetrahydrofuran	100 ml
Sodium metal	4.00 g
Reaction temperature	66°C
Reaction time	5 hr
Metallated monomer unit[a]	4.0 mole %

[a] Determined by Gilman's method.
[b] Calculated assuming metallation occurred at divinyl methylene.

TABLE VIII
Carboxylation of the Copolymer and *cis*-1,4-Polybutadiene

| Polymer | Solvent | Butyl lithium, mmole | Metallation reaction | | Carboxylated monomer unit, % |
			Temp., °C	Time, hr	
Acetylene–butadiene copolymer,[a] 1.18 g	toluene 75.1 ml	24.9	40	3	1.1
cis-1,4-Poly-butadiene,[b] 1.18 g	75.1 ml	24.9	40	3	0.0
Acetylene–butadiene copolymer,[a] 1.88 g	tetra-hydrofuran 87.5 ml	24.9	40	3	11.5
cis-1,4-Poly-butadiene,[b] 1.88 g	87.5 ml	24.9	40	3	0.0
Acetylene–butadiene copolymer,[a] 1.88 g	heptane 87.5 ml+ TMEDA[c] 24.9 mmole	24.9	80	1	23.0

[a] Acetylene content 24.0 mole %, $\overline{M}_n$, 2360.
[b] cis-1,4-, 81.2%; trans-1,4-, 15.9%; 1,2-, 2.9%; $\overline{M}_n$, 1990.
[c] Tetramethylethylenediamine.

and gradually turned to red or yellow, suggesting an anionic living polymerization to form graft copolymer. The graft polymers were completely soluble in benzene or chloroform.

Epoxidation of Copolymers

The acetylene–butadiene copolymer can be epoxidized by peracetic acid without gel formation as in the case of polybutadiene.[14] The epoxidation of the copolymer and polybutadiene is of almost same rate, as shown in Table IX.

The epoxidized copolymer can be cured by oxygen in an atmosphere of air,

TABLE IX
Epoxidation of the Polymer at 60°C for 2 hr[a]

Polymer	Acetic acid, mmole	Oxirane[e] oxygen, %	Epoxy equivalent of the product[e]
Acetylene–butadiene copolymer[b]	20	5.2	305.8
	30	7.6	226.7
	50	8.8	180.8
cis-1,4-Polybutadiene[c]	20	4.9	325.6
	40	8.7	184.5
1,2-Polybutadiene[d]	20	4.3	372.8
	40	6.7	238.2

[a] Polymer, 4.52 g; solvent, dichloroethane 50 ml; H_2O_2/acetic acid = 2 (molar ratio); amberlite IR 120/acetic acid = 1.52 (equivalent/mole).
[b] Acetylene content, 31.8 mole-%, $\overline{M}_n$, 2370.
[c] Polyoil Hüls 130; $\overline{M}_n$, 3200.
[d] Nippon Soda B 1000; $\overline{M}_n$, 1130.
[e] Determined by King's method.

TABLE X
Cure of Epoxidized Copolymer

Curing agent	Gelation time min	Heated time hr	Appearance of cured product
Maleic anhydride[a] 22.8 php	5	2	rigid resinous
Hexahydrophthalic anhydride[a] 35.8 php	30	17	rigid and somewhat elastic
m-Xylylene diamine[a] 31.6 php	30	19	rigid and somewhat elastic
$BF_3 \cdot (C_2H_5)NH_2$ complex[a] 2.0 php	10	20	rigid and somewhat elastic
Resorcinol[b] 25.0 php	15	20	rigid resinous
Glutaric acid[b] 30.0 php	10	20	rigid resinous

[a] Epoxidized copolymer: epoxy equivalent 215 from the copolymer containing 32.2 mole % acetylene and having $\bar{M}_n$ 2370; cure temperature, 100°C. php: Parts per 100 parts of epoxidized copolymer.

[b] Epoxidized copolymer: epoxy equivalent 221 from the copolymer containing 23.7 mole % acetylene and having $\bar{M}_n$ 1840; cure temperature, 130°C.

although the cure rate is somewhat slower than the nonepoxidized copolymer. The epoxidized copolymer mounted on a glass plate without epoxy curing agent is cured to form only the skin layer under heating at 100°C for 24 hr. However, the epoxidized copolymer of about 3 mm thickness was cured completely in the presence of epoxy curing agent as shown in Table X.

It is noteworthy that the epoxidized copolymer is more readily cured by the curing agents than the epoxidized polybutadienes as shown in Tables XI and XII.

Discussion

The mechanism of oxidation of drying oils was stated by Powers.[15] The steps encountered in the oxidation by air were believed to include peroxide formation, decomposition of peroxide, polymerization, and degradative oxidation. Recent work indicates the presence of hydroperoxide, cyclic peroxide, and epoxy-con-

TABLE XI
Cure of Epoxidized cis-1,4-Polybutadiene at 100°C[a]

Curing agent	Gelation time, hr	Heated time, hr	Appearance of cured product
Hexahydrophthalic anhydride 41.6 php	2	20	brittle
m-Xylylene diamine 36.8 php	more than 4	20	soft gel

[a] Epoxidized cis-1,4-polybutadiene: epoxy equivalent 185 from Polyoil Hüls 130 having $\bar{M}_n$ 3200.

TABLE XII
Cure of Epoxidized 1,2-Polybutadiene at $100°C^a$

Curing agent	Gelation time, hr	Heated time, hr	Appearance of cured product
Hexahydrophthalic anhydride 32.4 php	4	21	incompletely cured and very soft gel
m-Xylylene diamine 28.6 php	more than 4	21	incompletely cured

^{a} Epoxidized 1,2-polybutadiene: epoxy equivalent 238 from Nippon Soda B−1000 having $\bar{M}_n$ 1130.

taining structures.[3] According Farmer,[16,17] the initial addition of oxygen occurs at the double bond, and it is followed by radical formation and recombination as follows:

$$—CH_2—CH=CH— \ + \ O_2 \ \longrightarrow \ —CH_2—\overset{\cdot}{CH}—\underset{\underset{OO\cdot}{|}}{CH}—$$

$$—CH_2—\overset{\cdot}{CH}—\underset{\underset{OO\cdot}{|}}{CH}— \ + \ —CH=CH—CH_2—CH=CH— \ \longrightarrow$$

$$—CH_2—\overset{\cdot}{CH}—\underset{\underset{OOH}{|}}{CH}— \ + \ —CH=CH—\overset{\cdot}{CH}—CH=CH—$$

$$—\underset{\underset{O\cdot}{|}}{CH}— \ + \ —\underset{\underset{OO\cdot}{|}}{CH}— \ + \ —\underset{\underset{—CH—}{|}}{CH}— \ \longrightarrow \ —\underset{\underset{O}{|}}{CH}— \ + \ —\underset{\underset{\underset{—CH—}{|}}{\underset{O}{|}}}{CH}— \ + \ —\underset{\underset{\underset{—CH—}{|}}{\underset{\underset{O}{|}}{O}}}{CH}—$$

The allylic radical may be converted to a radical by a 1,3-shift like as in the case of methyl linoleate. The divinyl methylenes in this copolymer may favor the formation of allylic radical and give the high drying activity. The effect of residual catalysts in copolymers on the cure rate can be neglected, because the addition of small amounts of nickel naphthenate to copolymers did not accelerate the cure rate.

In Table II there are two kinds of polybutadiene, (d) and (e). However, similar polybutadiene showed a different cure tendency. The (d) kind possesses higher active methylene content than the (e) kind. High curing tendency of (d) may be due to the high active methylene content.

The addition of maleic anhydride (Manh) to the copolymers may be the ene-addition I and/or abnormal addition II rather than the Diels-Alder addition, as follows:

$$—CH=CH—CH_2—CH=CH— \ \xrightarrow{+Manh} \ —\overset{\cdot}{C}—CH=CH—CH=CH—$$

I

and / or

$$-CH=CH-CH_2-CH=CH- \xrightarrow{+Manh} -CH=CH-CH-CH=CH-$$

$$HC-CH_2$$
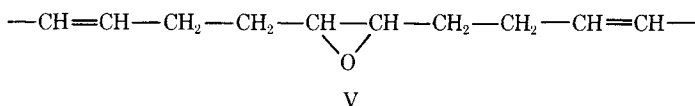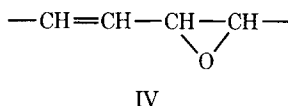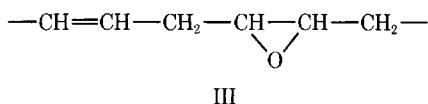
$$O=C \qquad C=O$$

$$O$$

II

If the reaction proceeds through scheme I or the Diels-Alder reaction, the conjugated double bond should be increased or decreased, respectively, as the reaction increases. However, NMR spectra indicate that the amount of conjugated double bond does not change in the course of the reaction. This fact suggests that the scheme II is plausible. The high reactivity of the copolymer towards maleic anhydride is due to the active methylene of divinyl methylene.

The main difference in the structure of the copolymer and cis-1,4-polybutadiene is that in the copolymer there are divinyl methylene arising from acetylene-butadiene linkage and a small amount of conjugated diene structure arising from acetylene-acetylene dyad. The conjugated double bond is not lithiated so readily by lithium metal like butadiene, isoprene, etc. The high reactivity of copolymer towards lithium may be due to the lithiation at the divinyl methylene proton as follows:

$$-CH=CH-CH_2-CH=CH-CH_2- \xrightarrow{Li}$$

$$-CH=CH-CH-CH=CH-CH_2- \rightleftharpoons HC\cdots CH$$

$$Li \qquad\qquad\qquad -HC \quad CH-$$
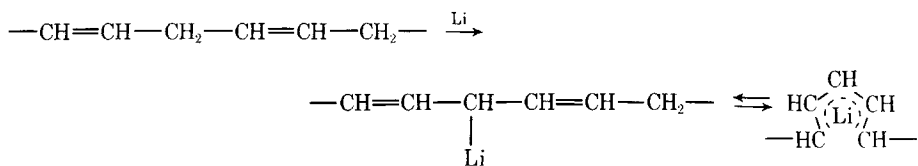
As described above, the epoxidized copolymer is more readily cured in the presence of curing agents than the epoxidized polybutadiene. The copolymer probably has allyl-epoxy III and vinyl-epoxy IV together with the epoxy groups isolated by two ethylene units V, while the polybutadiene has only the epoxy groups isolated by two ethylene units:

$$-CH=CH-CH_2-CH-CH-CH_2-$$

$$O$$

III

$$-CH=CH-CH-CH-$$

$$O$$

IV

$$-CH=CH-CH_2-CH_2-CH-CH-CH_2-CH_2-CH=CH-$$

$$O$$

V

The high curing ability of epoxidized copolymer may be due to the structure of epoxy groups represented mainly by III and IV.

References

1. B. Schleimer and H. Weber, *Angew. Makromol. Chem.,* **16/17,** 253 (1971).

2. M. Wismer and P. J. Prucnal, *Ind. Eng. Chem., Prod. Res. Develop.,* **10,** 279 (1971).

3. R. D. Singer, G. T. Williams, and G. Angerer, *Ind. Eng. Chem., Prod. Res. Develop.,* **10,** 287 (1971).

4. J. Furukawa, E. Kobayashi, and T. Kawagoe, *J. Polym. Sci.,* **B11,** 573 (1973).

5. J. Furukawa, E. Kobayashi, and T. Kawagoe, *J. Polym. Sci., Polym. Chem. Ed.,* to be published.

6. J. Furukawa, T. Kawagoe, and E. Kobayashi, *J. Polym. Sci., Polym. Chem. Ed.,* **14,** 1213 (1976).

7. J. S. Fritz and N. M. Lisicki, *Anal. Chem.,* **23,** 589 (1951).

8. H. Gilman and F. K. Cartledge, *J. Organometal Chem.,* **2,** 447 (1964).

9. G. King, *Nature,* **164,** 706 (1949).

10. A. J. Durbetaki, *Anal. Chem.,* **28,** 2000 (1956).

11. J. Böeseken and R. Hoevers, *Rec. Trav. Chim.,* **49,** 1165 (1930); E. T. Clocker, U.S. Pats. 2,188,882, 2,188,883, and 2,188,890 (1940).

12. H. M. Hoogsteen and A. E. Young, *Ind. Eng. Chem.,* **42,** 1587 (1950).

13. H. Harada, K. Shiina, and Y. Minoura, *Kōgyo Kagaku Zasshi,* **69,** 337, 2194, 2320 (1966).

14. H. S. Makowshi, M. Lynn, and D. H. Rotenberg, *J. Macromol. Sci.,* **A4**(7), 1563 (1970).

15. P. O. Powers, *Ind. Eng. Chem.,* **41,** 304 (1949).

16. E. H. Farmer and A. Sandralingam, *J. Chem. Soc.,* 121 (1942).

17. E. H. Farmer and D. A. Sutton, *J. Chem. Soc.,* 119 (1943).