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Hidemasa Okamoto[a][b]; Shoichi Adachi[a]; Tadashiiwai[a]
[a] Central Research Laboratory, Ube Industries Ltd., Yamaguchi, Ube, Japan [b] Hirakata Plastics Laboratory, Ube Industries Ltd., Hirakata, Osaka, Japan

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Radiation-Induced Addition Reaction of Ethyl Mercaptan and Carbon Tetrachloride to 1,2-Polybutadiene

HIDEMASA OKAMOTO,* SHOICHI ADACHI, and TADASHI IWAI

Central Research Laboratory
Ube Industries, Ltd.
Ube, Yamaguchi 755, Japan

ABSTRACT

γ-Ray-induced addition reactions of syndiotactic 1,2-polybutadiene film with various compounds were carried out at room temperature. The weight of the film markedly increased when ethyl mercaptan was used. In the reaction with ethyl mercaptan, only addition took place without crosslinking. The addition of ethyl mercaptan to the vinyl group of syndiotactic 1,2-polybutadiene followed anti-Markownikoff rule, and gave a 1:1 addition product. The rate of addition increased as the crystallinity of syndiotactic 1,2-polybutadiene used became lower. A similar relation between the crystallinity and the rate of addition was also observed in the γ-ray-induced addition of carbon tetrachloride to syndiotactic 1,2-polybutadiene, but at the same time gelation was pronounced. When liquid 1,2-polybutadiene was used instead of syndiotactic-1,2-polybutadiene, gelation which made the polymer insoluble in carbon tetrachloride did not take place, although a crosslinking reaction was noted. The appearance of the product in this case changed from a

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*Present address: Hirakata Plastics Laboratory, Ube Industries, Ltd., Hirakata, Osaka 573, Japan.

viscous liquid to a white powder as the reaction proceeded. The addition of carbon tetrachloride to the vinyl group of liquid 1,2-polybutadiene was also of the anti-Markownikoff type. This addition was accompanied by unexpectedly large vinyl consumption. The total decrease in vinyl group was found to be much larger than the decrease in vinyl group which was brought about by the addition of carbon tetrachloride. This discrepancy was attributed to cyclization and crosslinking reactions which were ascribed to the vinyl group bound by the main chain.

INTRODUCTION

1,2-Polybutadiene is considered to have a higher reactivity due to its pendent vinyl group in comparison with 1,4-polybutadiene which has internal double bonds in the main chain. In the previous paper [1], the effect of radiation on syndiotactic 1,2-polybutadiene was studied, and it was found that crosslinking and cyclization took place very easily. Another radiation-induced modification of 1,2-polybutadiene which utilizes its vinyl group is the addition reaction of low molecular weight compounds to the vinyl group. The addition reaction to the vinyl group of this polymer may become a chain reaction when a suitable compound is used. That is to say, if 1,2-polybutadiene is regarded as a taxogen as vinyl monomers in telomerization, some kinds of compounds can become effective telogens for this polymer. From a similar point of view, addition reactions of mercaptans [2-4] and carbon tetrachloride [5] to 1,4-polybutadiene have been studied.

In the present paper, addition reactions of ethyl mercaptan and carbon tetrachloride to 1,2-polybutadiene are carried out with the use of γ-rays, and the structures of the products were investigated in some detail.

EXPERIMENTAL

Materials

1,2-Polybutadienes used were syndiotactic 1,2-polybutadiene (syndio-1,2-PB) and liquid 1,2-polybutadiene (liquid 1,2-PB) of which some characteristics are summarized in Table 1. Vinyl contents of 1,2-PB were determined by infrared spectrometry according to the method of Morero et al. [8] and NMR spectrometry.

TABLE 1. Some Characteristics of Syndio-1,2-PB and Liquid 1,2-PB

Polymer	$\overline{M_n}$	Melting point (°C)	Vinyl content (%)	Degree of crystallinity (%)[a]	Trans-1,4 content (%)	Preparation
Syndio-1,2-PB		192	93.7	65		Sugiura et al. [6]
		141	83.5	45		Sugiura et al. [7]
		90	98.0	25		Commercial (Japan Synthetic Rubber Co.)
Liquid 1,2-PB	1050		91.2		8.8	Commercial (NISSO-PB,B-1000)

[a] Degree of crystallinity was determined by x-ray diffraction.

Syndio-1,2-PB was used in the form of films (20 × 50 × 0.17 mm) which contained no antioxidant. $SiHCl_3$, $SiCl_4$, and C_2H_5SH of commercially guaranteed grade were used without further purification. Other chemicals were purified by distillation.

Procedure

About 1 g of syndio-1,2-PB film or liquid 1,2-PB and 20 ml of low molecular weight compound were introduced into a glass ampoule, which was then connected to a vacuum line, degassed at liquid nitrogen temperature by the freeze-thaw method, and sealed off. The ampoule was irradiated by ^{60}Co γ-rays at ca. 20°C. The absorbed dose was estimated from the exposure dose by correcting the electron density of the reaction system [9]. After irradiation, the contents of the ampoule were poured into 100 ml of methanol. The film or the precipitated polymer was collected, washed with methanol, and dried in vacuo at 40°C until constant weight was reached. In the case of syndio-1,2-PB film, the gel fraction of the product was measured in the same manner described in the previous paper [1].

Characterization

Elemental analysis on S of the C_2H_5SH addition product was carried out by using a Yanagimoto MX-3 elemental analysis apparatus, and that on Cl of the CCl_4 addition product was performed according to the bomb method. Infrared spectra were recorded in the form of films with 20 μ thickness for the C_2H_5SH addition product, and 2 wt/vol % CCl_4 and CS_2 solutions for the CCl_4 addition product by using a 0.5 mm thick fixed cell on a Hitachi EPI-2 infrared spectrometer. NMR spectra were taken by the use of a Japan Electronics JNM 4H-100 spectrometer in 5% (w/v) o-dichlorobenzene solution for the C_2H_5SH addition product and CS_2 solution for the CCl_4 addition product, respectively. Tetramethylsilane was used as an internal standard. The number-average molecular weight $\overline{M}_n$ of the CCl_4 addition product started from liquid 1,2-PB was determined with a Hitachi 115 molecular weight apparatus in benzene as a solvent at 40° C.

RESULTS AND DISCUSSION

Reaction of Syndio-1,2-PB with Various Compounds

Table 2 shows results of reaction between syndio-1,2-PB film with 65% crystallinity and various compounds by γ-rays. The film was insoluble in all compounds employed and the reaction was carried out

TABLE 2. Results of Reaction between Syndio-1,2-PB Film of 65% Crystallinity and Various Compounds by γ-Radiation[a]

Compounds	Weight increase (%)	Gel fraction (%)
-	0.0	69.2
CH_2Cl_2	0.0	46.0
$CHCl_3$	2.1	44.8
CCl_4	8.5	77.8
CF_2Cl_2	2.5	76.7
$CFCl_3$	4.7	83.8
$(CH_3)_2CHOH$	0.3	52.5
$ClCH_2CH_2OH$	0.0	68.3
$HCONH_2$	1.8	55.6
$SiHCl_3$	9.4	98.0
$SiCl_4$	4.2	76.2
C_2H_5SH	15.4	0.4

[a] Reaction conditions: syndio-1,2-PB film, 1 g; compound, 20 ml; dose rate, 0.09 Mrad/hr; temperature, ca. 20°C; time, 7 hr.

in the heterogeneous phase during the course of irradiation. Without compound, i.e., on irradiation in vacuo, crosslinking is observed as a result of the radiation effect, as reported in the previous paper [1]. Table 2 indicates that CCl_4, CF_2Cl_2, $CFCl_3$, $SiHCl_3$, and $SiCl_4$ not only add to syndio-1,2-PB but also promote the crosslinking reaction. On the other hand, C_2H_5SH adds much faster than other compounds without bringing about crosslinking.

Addition reactions of C_2H_5SH and CCl_4 were thus investigated in some detail.

Addition Reaction of C_2H_5SH to Syndio-1,2-PB

Figure 1 shows the change in infrared spectrum of syndio-1,2-PB film with 65% crystallinity in the reaction with C_2H_5SH by γ-radiation. Upon irradiation, the bands at 3080, 1840, 1640, 1415, 995, and 910 cm^{-1} due to the vinyl group decrease, and those at 2990-2860 and

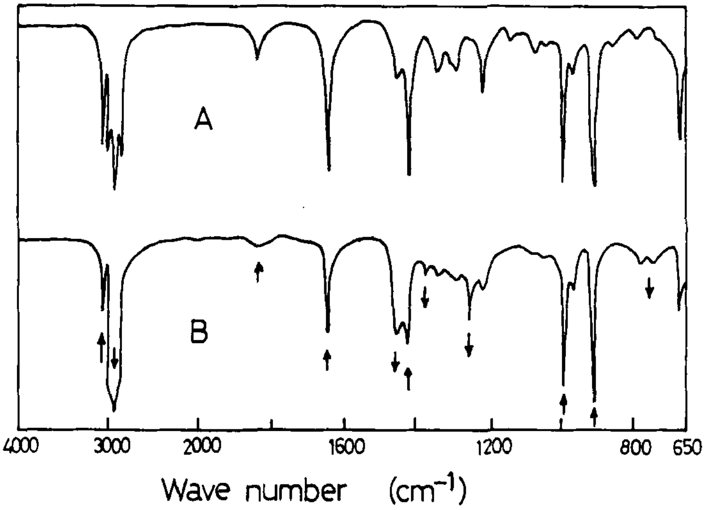


FIG. 1. Change in infrared spectrum of syndio-1,2-PB film with 65% crystallinity in the reaction with C_2H_5SH by γ-radiation: (A) unirradiated; (B) irradiated (0.09 Mrad/hr for 39 hr = 3.51 Mrad), 37.4% weight increase.

1460 cm^{-1} due to CH_2 increase. In addition, new bands appeared at 1375 cm^{-1} and 1257 and 780-740 cm^{-1} which are ascribed to CH_3 and S-CH_2, respectively. The latter bands were identified by comparison with the spectra of n-$C_4H_9SC_2H_5$ and (iso-$C_4H_9)_2S$. The above changes indicate that the addition of C_2H_5SH takes place at the vinyl group of syndio-1,2-PB.

The change in the NMR spectrum is shown in Fig. 2. Each peak was assigned by taking into consideration that the original polymer had some 1,4-units, mostly trans-1,4, as shown in Fig. 1. Newly appearing peaks at 8.35 and 7.40 ppm were identified by reference to the spectra of such sulfides [10] as $C_2H_5SCH_3$, (n-$C_3H_7)_2S$, and n-$C_5H_{11}SCH_3$ and of polypropylene [11]. Assignments of the peaks are indicated in structure I. These assignments indicate that the addition of C_2H_5SH to the vinyl group follows an anti-Markownikoff rule as for radiation-induced addition reactions of C_2H_5SH to olefins [12]. This suggests that the addition proceeds by a radical mechanism. When addition yield of C_2H_5SH is defined as the ratio of double bonds added by C_2H_5SH to original double bonds, this can be determined by the weight increase, the S content of the product, and also by the above NMR spectrum. Comparison of addition yields measured

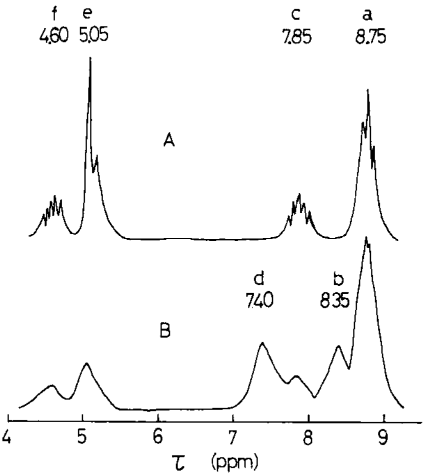
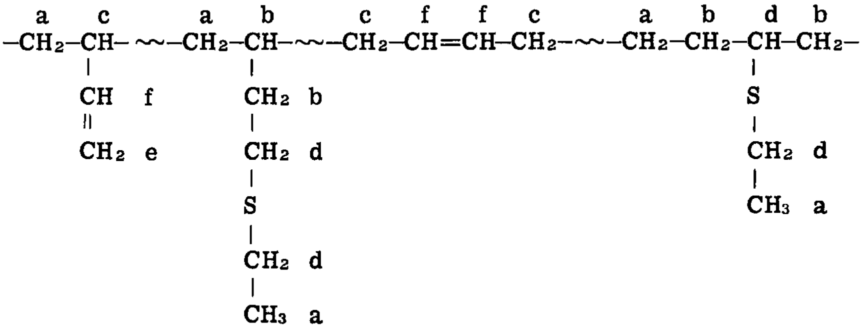


FIG. 2. Change in NMR spectrum of syndio-1,2-PB film with 65% crystallinity in the reaction with C_2H_5SH by γ-radiation: (A) unirradiated; (B) irradiated (0.09 Mrad/hr for 39 hr = 3.51 Mrad), 37.4% weight increase.



$$\begin{array}{ccccccc}
\text{a} & \text{c} & \text{a} & \text{b} & \text{c}\quad\text{f}\quad\text{f}\quad\text{c}\qquad\text{a}\quad\text{b} & \text{d} & \text{b} \\
-CH_2- & CH & -\sim\sim-CH_2- & CH & -\sim\sim-CH_2-CH=CH-CH_2-\sim\sim-CH_2-CH_2- & CH & -CH_2- \\
 & | & & | & & | & \\
 & CH\ \ \text{f} & & CH_2\ \ \text{b} & & S & \\
 & \| & & | & & | & \\
 & CH_2\ \ \text{e} & & CH_2\ \ \text{d} & & CH_2\ \ \text{d} & \\
 & & & | & & | & \\
 & & & S & & CH_3\ \ \text{a} & \\
 & & & | & & & \\
 & & & CH_2\ \ \text{d} & & & \\
 & & & | & & & \\
 & & & CH_3\ \ \text{a} & & &
\end{array}$$

I

by the three methods is shown in Table 3, where addition yields obtained are in good agreement with each other. This fact suggests that C_2H_5SH gives 1:1 addition products.

Figure 3 shows effect of crystallinity of syndio-1,2-PB film on addition yield. The addition reaction proceeded in heterogeneous phase throughout the irradiation in the case of 65% crystallinity as

TABLE 3. Comparison of Addition Yield of C_2H_5SH Measured by Several Methods

Dose (Mrad)	Addition yield of C_2H_5SH (%)		
	From weight increase	From NMR	From S content
0.63	13.4	13.6	12.9
1.44	23.7	23.4	21.8
3.51	32.6	35.6	33.2

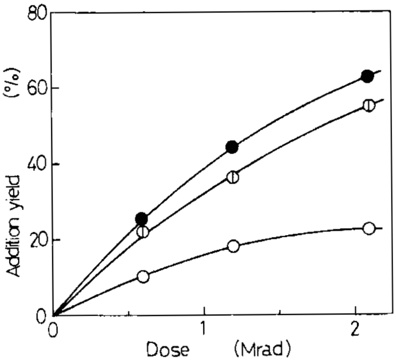


FIG. 3. Effect of crystallinity of syndio-1,2-PB on addition yield of C_2H_5SH: (○) 65% crystallinity; (⦶) 45%; (●) 25%. Syndio-1,2-PB film, 1 g; C_2H_5SH, 20 ml; dose rate, 0.3 Mrad/hr; temperature, ca. 20°C.

already described. In the case of 45% crystallinity, the film swelled or dissolved in C_2H_5SH as the reaction proceeded. Moreover, the film with 25% crystallinity dissolved before irradiation, and the reaction was carried out in homogeneous phase. The rate of addition increases as the crystallinity decreases. This means that the rate of addition depends greatly on diffusion of C_2H_5SH into the film.

Addition Reaction of CCl_4 to Liquid 1,2-PB

By analogy with the results given in Fig. 3, when syndio-1,2-PB of low crystallinity is used, CCl_4 is also expected to add rapidly to

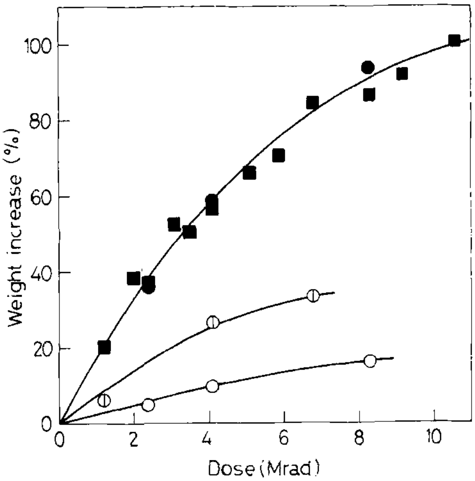


FIG. 4. Reaction with CCl_4 by γ-radiation of syndio-1,2-PB film with the crystallinity of 65% (○), 45% (⦶) or 25% (●), or liquid 1,2-PB (■). 1,2-PB, 1 g; CCl_4, 20 ml; temperature, ca. 20°C; dose rate, 0.59 Mrad/hr.

this polymer. Various syndio-1,2-PB films were irradiated in CCl_4 at ca. 20°C. Films with crystallinities of 65 and 45% did not dissolve in CCl_4, and the addition reaction was carried out in heterogeneous phase throughout the irradiation. In the case of film with 25% crystallinity, a homogeneous CCl_4 solution was obtained before irradiation but gelation of the solution took place upon irradiation. As shown in Fig. 4, the weight of the film increases with dose, and, as expected, the rate of weight increase becomes higher as the crystallinity decreases. On the other hand, a high gel fraction (more than 90%) was attained in each film. This suggests that CCl_4 not only adds to syndio-1,2-PB but also accelerates crosslinking reaction as already mentioned.

Because of the high gel fractions, characterization of the above products seems quite difficult. In general, gelation becomes slower as the molecular weight of the polymer decreases, so liquid 1,2-PB was employed as low molecular weight 1,2-PB instead of the high molecular weight syndio-1,2-PB. Liquid 1,2-PB was soluble in CCl_4 before irradiation, and no gelation was observed by irradiation. Appearance of the products changed from a viscous liquid to a white powder when the weight increase was beyond ca. 55%. As shown in Fig. 4, the rate of weight increase is nearly equal to that in syndio-1,2-PB with 25% crystallinity. Thus, addition of CCl_4 to liquid 1,2-PB occurs easily without gelation, as expected.

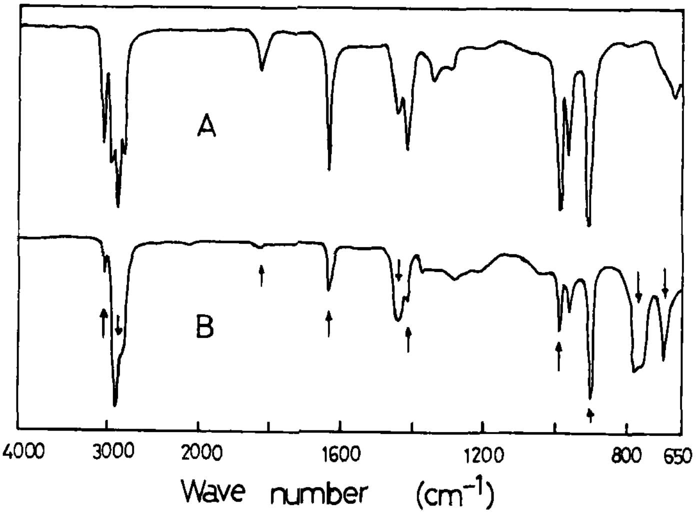


FIG. 5. Change in infrared spectrum of liquid 1,2-PB in the reaction with CCl_4 by γ-radiation: (A) unirradiated; (B) irradiated (4.1 Mrad), 56.7% weight increase.

The change in the infrared spectrum of liquid 1,2-PB by the addition of CCl_4 is shown in Fig. 5. With the addition of CCl_4, vinyl bands at 3080, 1840, 1640, 1415, 995, and 910 cm^{-1} decrease, and CH_2 bands at 2990-2860 and 1460 cm^{-1} increase. Further, new bands appear, at 780-760 and 695 cm^{-1} which are attributable to the C–Cl bond. According to Kharasch et al. [13], an anti-Markownikoff type 1:1 adduct is formed in the radical telomerization of 1-octene with excess CCl_4. Comparison of the infrared spectrum of our product with that of the 1:1 adduct of 1-octene and CCl_4 showed that the bands attributed to C–Cl in our product were similar to those of the above 1:1 adduct. This indicates that the addition of CCl_4 to the vinyl group of liquid 1,2-PB is also anti-Markownikoff type. In other words, this addition reaction is considered to be a radical reaction. This concept was supported by the fact that a similar product had been obtained by using benzoyl peroxide as a radical initiator in the reaction of liquid 1,2-PB with CCl_4.

The addition yield of CCl_4, defined as the ratio of double bonds added by CCl_4 to original double bonds, is determined by the weight increase or the Cl content of the product. On the other hand, the consumption of the vinyl group, which occupies a large portion of the double bonds, can be obtained from the infrared spectrum by using calibration curves between vinyl concentration and absorbancies of

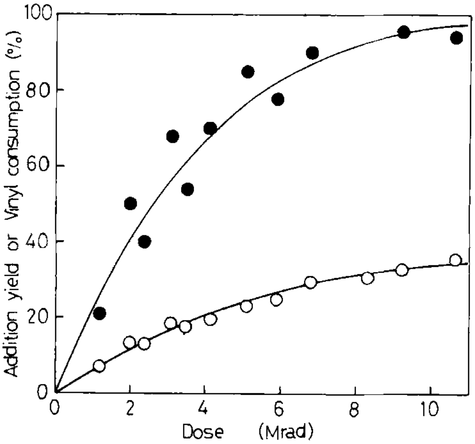


FIG. 6. Relations between (○) dose and addition yield of CCl_4 and (●) between dose and vinyl consumption in the addition reaction of CCl_4 to liquid 1,2-PB. Liquid 1,2-PB, 1 g; CCl_4, 20 ml; temperature, ca. 20° C; dose rate, 0.59 Mrad/hr.

the appropriate vinyl bands. Figure 6 shows the relations between dose and addition yield, and between dose and vinyl consumption. Addition yields determined by the above two methods were approximately equal. It is found that vinyl consumptions are markedly larger than addition yields. Vinyl consumption reaches more than 90% at the addition yield of ca. 30%. Compared with the above 1-octene as a low molecular weight model compound for liquid 1,2-PB, the discrepancy between addition yield and vinyl consumption is characteristic. This suggests that other reactions which consume vinyl groups also take place together with the addition of CCl_4. Presumably they are crosslinking and cyclization.

The change in NMR spectrum of liquid 1,2-PB on the addition of CCl_4 is given in Fig. 7. With the addition of CCl_4, the peaks due to double bonds at 5.05 and 4.7 ppm decrease, and new peaks appear at 7.3 and 6.4 ppm. Compared with the spectra of the 1:1 adduct of 1-octene-CCl_4 [14] and ethylene-CCl_4 telomers [15], the peaks at 7.3 and 6.4 ppm can be assigned to the protons of $-CH_2CCl_3$ and $-CHCl-$, respectively. Further, an increase in the peak at 8.7-8.0 ppm may be ascribed to a cyclized, crosslinked structure. Crosslinking is confirmed by the molecular weight measurement which is described later. Thus, the CCl_4 addition product is considered to have the structure II:

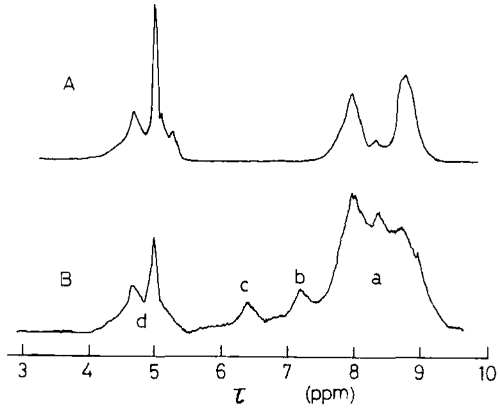
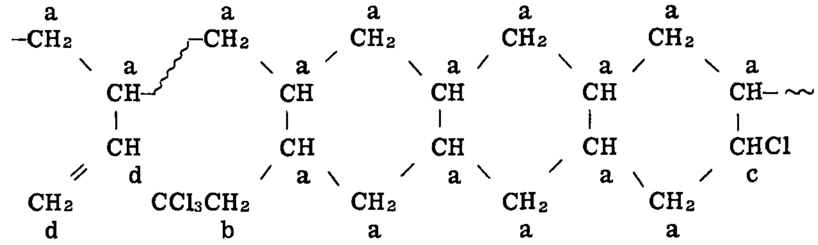
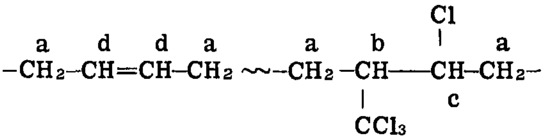


FIG. 7. Change in NMR spectrum of liquid 1,2-PB in the reaction with CCl_4 by γ-radiation: (A) unirradiated; (B) irradiated (4.1 Mrad), CCl_4 addition yield of 19.9%.





$$-\overset{a}{CH_2}-\overset{d}{CH}=\overset{d}{CH}-\overset{a}{CH_2}\sim\overset{a}{CH_2}-\underset{\displaystyle CCl_3}{\underset{|}{\overset{b}{CH}}}-\underset{c}{\overset{\overset{Cl}{|}}{CH}}-\overset{a}{CH_2}-$$

II

where crosslinked structure is neglected. This shows apparently CCl_4 added structure across cyclized and crosslinked structure.

On the basis of these assignments, addition of CCl_4 as well as cyclization and crosslinking can be estimated quantitatively. At first, the contents of 1,2- and 1,4-unit of the original polymer are defined as α and β, respectively ($\alpha = 0.912$, $\beta = 0.088$). On putting x and y as the contents of 1,2- and 1,4-unit consumed by CCl_4 addition, respectively, and z as the content of 1,2-unit consumed by cyclization and crosslinking, the area of each peak (S) is given by Eq. (1):

$$\begin{aligned} S_a k &= 3(\alpha - x - z) + 3x + 6z + 4(\beta - y) + 4y = 3\alpha + 4\beta + 3z \\ S_b k &= 2x + y \\ S_c k &= x + y \\ S_d k &= 3(\alpha - x - z) + 2(\beta - y) = 3\alpha + 2\beta - 3x - 2y - 3z \end{aligned} \tag{1}$$

where the subscripts of S stand for the peaks shown in Fig. 7 and k is a constant. By solving Eq. (1) by the method of least squares, x, y, and z are obtained in the product given in Fig. 7: $x = 0.165$, $y = 0.038$, $z = 0.452$. From these results, addition yield and vinyl consumption defined above are given by $x + y$ (0.203) and $(x + z)/\alpha$ (0.677), respectively. These values are in fair agreement with those determined by the weight increase or the Cl content (0.199) and infrared spectrum (0.698), respectively. These facts indicate that the above assignment is reasonable. Further, with respect to 1,2-unit the ratio of cyclization and crosslinking to addition is given

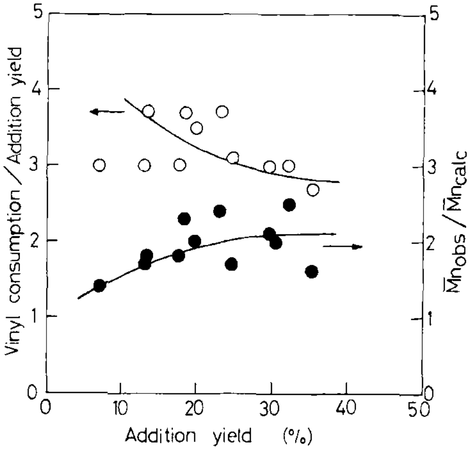


FIG. 8. Relations between (○) addition yield of CCl_4 and vinyl consumption/addition yield and (●) between addition yield of CCl_4 and $\overline{M}n_{obs}/\overline{M}n_{calc}$.

by z/x (2.74), which implies that the cyclization and crosslinking is much faster than the addition. Cyclization and crosslinking may be ascribed to the vinyl groups bound by the main chain of liquid 1,2-PB. That is to say, the motion of the vinyl group is not free as 1-octene but restricted by the main chain.

The ratio of vinyl consumption to addition yield, which signifies the number of vinyl groups disappeared by a single addition of CCl_4 to vinyl groups, decreases gradually with addition yield as shown in Fig. 8. This decrease with addition yield can be explained as follows. Cyclization which followed addition of $CCl_3\cdot$ to the vinyl group is more disturbed in the later stages than in the early stages, since the probability of an adjacent vinyl group to convert already cyclized structure increases in the later stages. Figure 8 also shows change in $\overline{M}n_{obs}/\overline{M}n_{calc}$, where $\overline{M}n_{calc}$ is the $\overline{M}_n$ calculated by assuming that only addition of CCl_4 takes place in this system. From the value of $\overline{M}n_{obs}/\overline{M}n_{calc}$, it can be said that crosslinking reaction also takes place, as in the case of the addition of CCl_4 to syndio-1,2-PB, and the CCl_4 addition product consists of about two molecules of the original polymer in the later stage. Due to the comparatively low $\overline{M}_n$ of liquid 1,2-PB used, this crosslinking reaction is not extensive enough to bring about gelation.

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