Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Investigation of Conversion of Styrene and Fumarate Double Bonds in Unsaturated Polyester Resins

Kahei Sakaguchi[a]
[a] Kao-Atlas Laboratories, Wakayama, Shi, Japan

To cite this Article Sakaguchi, Kahei(1974) 'Investigation of Conversion of Styrene and Fumarate Double Bonds in Unsaturated Polyester Resins', Journal of Macromolecular Science, Part A, 8: 3, 477 — 498

To link to this Article: DOI: 10.1080/00222337408065845

URL: http://dx.doi.org/10.1080/00222337408065845

J. MACROMOL. SCI.—CHEM., A8(3), pp. 477-498 (1974)

Investigation of Conversion of Styrene and Fumarate Double Bonds in Unsaturated Polyester Resins

KAHEI SAKAGUCHI

Kao-Atlas Laboratories
Wakayama-Shi, Japan

ABSTRACT

The conversion of styrene and fumarate double bonds in the copolymerization of unsaturated polyesters and styrene was investigated. Several commercial polyester resins including Bisphenol-type, Iso-type and G-type resins were used. The initial fumarate double bond, the equivalent double bond per 100 g of the polyesters, was determined by the hydrogenation procedure which was developed for the present study. Using palladium-carbon catalyst and benzene-acetone (1:1) mixture, polyester resin can be hydrogenated satisfactorily.

The cured resin was extracted with chloroform. The styrene in the chloroform was determined by ASTM D-1159, bromine index method. The conversion of the fumarate double bond was calculated from the soluble part of polyester resin using the theoretical equations which were derived from the basic theory of Flory. The validity of the equations was examined by application of Funke et al.'s experimental results and found to be satisfactory. With the confidence of these results, commercial polyester resins were investigated to determine

the effect of the condition of polymerization on the conversion of styrene and fumarate double bonds.
For all the polyesters the conversion of styrene was at least over 80% after a room temperature cure of 24 hr with a dimethyl anilin-cobalt naphthenate-methyl ethyl ketone peroxide three component catalyst system, and it reached approximately 100% after postcure of 100°C for 2 hr. On the other hand, the conversion of the fumarate double bond depended greatly upon the type of the resin. Bisphenol-type resin gave the highest conversion, and the conversion for Iso-type resin was higher than that for G-type resin. In the case of Bisphenol-type resin, there was no difference in the conversion of fumarate double bond between the room temperature cure and the postcure, but the conversions of fumarate double bond for G- and Iso-type resins were increased remarkably by postcure. The Barcol hardness is applicable to determine the conversion of styrene for the specified polyesters based on the relationship between the conversion of styrene and the Barcol hardness.

INTRODUCTION

The Barcol hardness meter has been conveniently used for the inspection of the extent of the degree of cure on unsaturated polyester resin. However, this portable instrument did not give precise values when many factors were varied. In order to obtain absolute values, we have determined the conversion of styrene, C_S, and the conversion of fumarate double bond, C_F, by chemical analysis. The conversion of styrene can be easily determined by the titration of solvent extract. On the other hand, the conversion of fumarate double bond was difficult to determine by the ordinary method. Funke et al. [1] have proposed the determination of the conversion of the fumarate double bond by analysis of the copolymer obtained after an alkaline hydrolysis of the cured resin. They have studied this subject extensively [2-5], and Ghanem [6], Bohdanecký et al. [7], and Demmler [8] have developed the work of Funke et al. Unfortunately, Funke's method is not applicable to a Bisphenol-type polyester resin because the cured resin can hardly be decomposed by alkaline hydrolysis. Hence, we have derived an equation based on the basic theory proposed by Flory [9] to determine the conversion of fumarate double bond from the amount of the soluble part in the cured polyester resin. Funke et al.'s experimental results [1, 2] were applied to the present equation and were found to be satisfactory, i.e., the conversion of fumarate double bond by Funke et al. [1, 2] was in good agreement with the calculated conversion of fumarate double bond, q.

The major object of this study was to determine the conversions of styrene and fumarate double bonds for commercial polyester resins and to examine the effect of the type of resins, the cure time, and the cure conditions on the conversions of styrene and fumarate double bonds in the polymerization process.

THEORY

Flory [9] has presented the "most probable distribution" for linear condensation polymers prepared from the esterification of equimolar dibasic acid and glycols:

$$W_x = x(1 - P)^2 P^{x-1} \tag{1}$$

where W_x is the weight fraction of the molecules containing x units, x is the number of units in a molecule, and P is the extent of reaction which is defined by

$$\bar{x} = \frac{1}{1 - P} \tag{2}$$

where $\bar{x}$ is the number-average degree of polymerization.

In the present treatment the polyester chain is a linear condensation product of glycols and unsaturated dicarboxylic acids in combination with or without saturated dicarboxylic acids, and the polymerization process of polyester with styrene fulfills the following conditions:

1. There must be a fumarate double bond per unit of a polyester chain.
2. The soluble polyester chain does not contain any cross-linked units, i.e., all the fumarate double bond in a chain must remain unreacted.
3. The reactivity ratio of the fumarate double bond must be constant during the whole polymerization process.

Now, let q be the probability of cross-linking of a fumarate double bond. The probability that a fumarate double bond does not react is given by 1 - q. Thus the probability that all x-units in a molecule do not cross-link is $(1 - q)^x$, because each units have an independent probability. After the copolymerization of unsaturated polyester with styrene, the weight fraction of unsaturated polyester, all of whose fumarate double bond is not cross-linked, is given by $W_x(1 - q)^x$. Thus the soluble fraction in the cured resin is given by

$$W = \sum_{x=1}^{\infty} W_x(1 - q)^x \tag{3}$$

The number-average degree of polymerization $\bar{x}$ can be calculated by

$$\bar{x} = \bar{M}_n/\bar{M}_0 \tag{4}$$

where $\bar{M}_n$ is the number-average molecular weight of the primary polyester molecule, and, especially in the present paper, $\bar{M}_0$ is defined as the number-average molecular weight per unit containing one fumarate double bond. $\bar{M}_n$ can be determined by end-group analysis, acid number, and hydroxyl number:

$$\bar{M}_n = \frac{56.108 \times 2000}{\text{acid number} + \text{hydroxyl number}} \tag{5}$$

Figure 1 shows typical curves of "most probable distribution" for a linear polyester. Figure 2 shows the relationship between $(1 - q)^x$ and x. Figure 3 shows the relationship between $W_x(1 - q)^x$ and x, and Fig. 4 shows the relationship between q and W. W is determined experimentally by extracting the cured resin with chloroform, and the conversion of fumarate double bond, q, can be calculated from the relationship in Fig. 4.

VALIDITY OF EQUATIONS

Funke et al. [1, 2] have extensively determined the conversion of fumarate double bond C_F by chemical analysis. They have also determined the amount of soluble part, W, in the cured resin. These results were used to examine the present equations. The experimental results by Funke et al. [1, 2] and the conversion of the fumarate double bond q calculated from the present equations are shown in Tables 1 and 2. They have prepared the polyester resins from maleic anhydride, adipic acid, and 1,4-butylene glycol, and the resin was dissolved in styrene and cured with benzoyl peroxide-dimethyl anilin

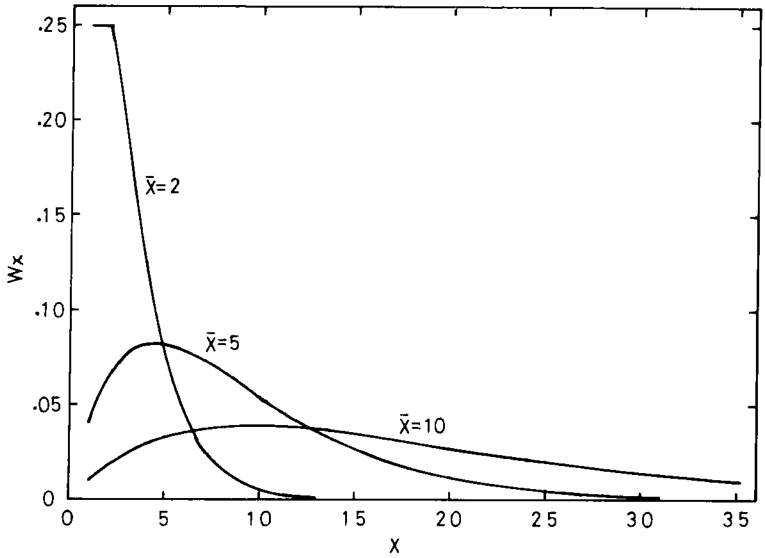

FIG. 1. The typical curves of "most probable distribution" for a linear polyester.

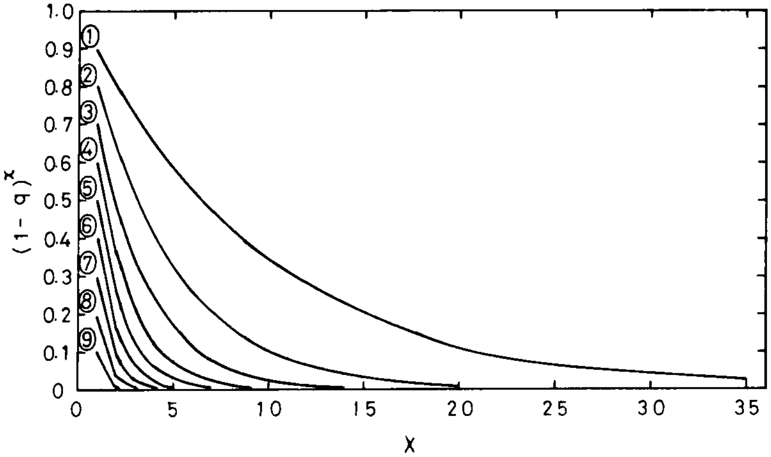

FIG. 2. The relationship between $(1 - q)^x$ and x. The q values are one-tenth of the curve numbers.

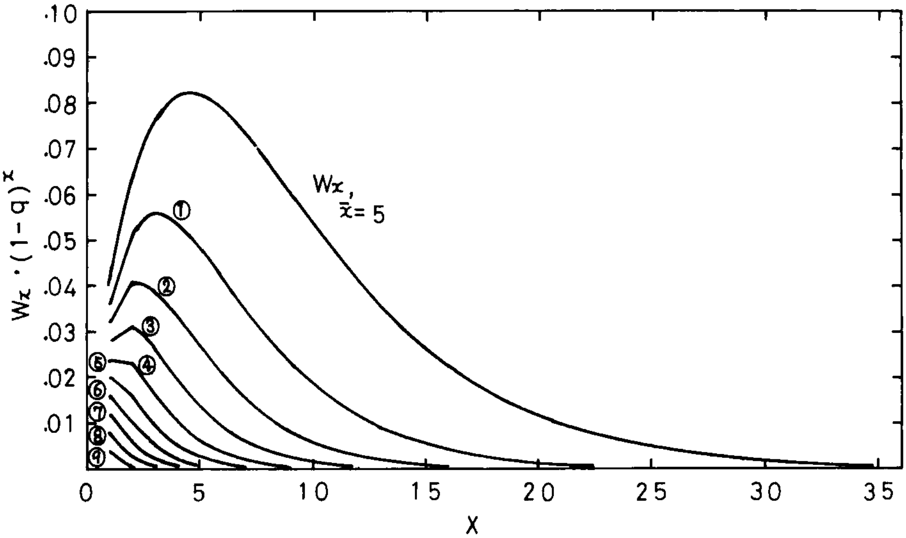

FIG. 3. The relationship between W_x $(1 - q)^x$ and x. The q values are one-tenth of the curve numbers.

at 20°C at first and post-cured at elevated temperatures. The cured resin was extracted with benzene and the resinous solid in the extract was obtained after evaporation of benzene. As they did not give the number-average molecular weight for the polyesters, we used the expected hydroxyl number which was twice the acid numbers. Funke's results [1] have been examined by Shito [10], and comparison with the present examination is shown in Fig. 5. It is obvious that the conversion of fumarate double bond C_F as determined by Funke et al. [1] is in good agreement with the conversion of fumarate double bond q calculated by the present equations. The soluble part W in Table 2 is the value corrected by the saponification number of the soluble part, so the conversion of the fumarate double bond C_F found coincides more exactly with the conversion of fumarate double bond q calculated.

EXPERIMENTAL

Analysis of Unsaturated Polyester Resins

Several commercial polyester resins, including Bisphenol-type, Iso-type and G-type resins, were used in this study. Their chemical

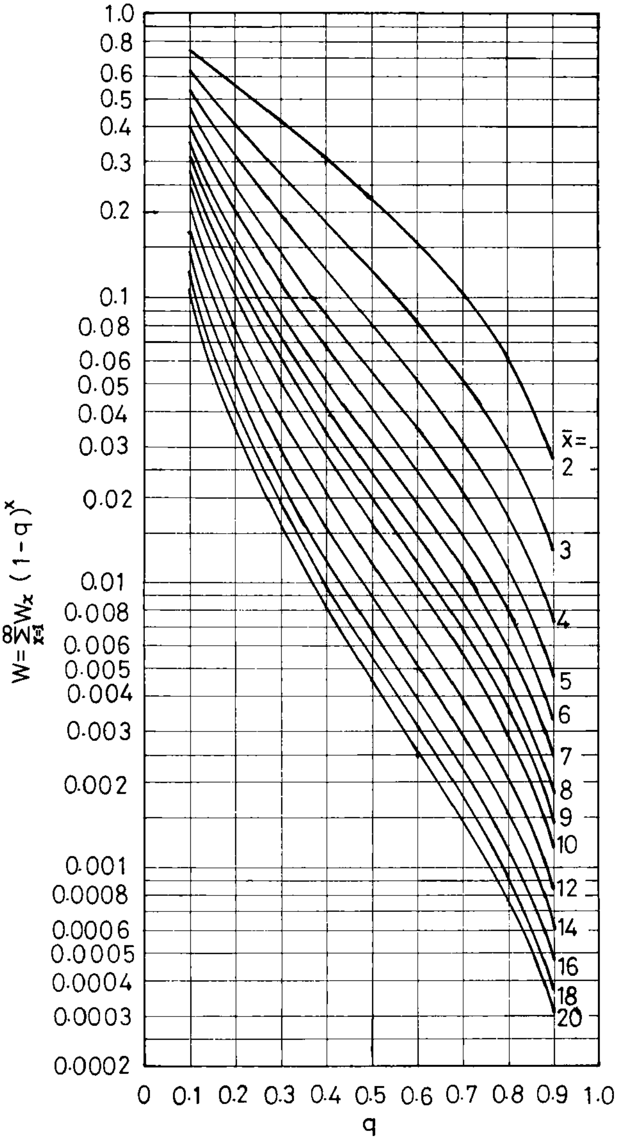

FIG. 4. The relationship between W and q.

TABLE 1. Examination of Funke's Results[a]

Resin			Polyester									Cured resin			
	Styrene		Mole ratio									C_S	C_F	W	q
No.	Wt%	Mole fraction	MA	AA	BD	Equivalent of double bond/100 g	$\overline{M}_0$	Acid No.	Hydroxyl No.	$\overline{M}_n$	$\overline{x}$	(mole %)	(mole %)	(mole %)	(mole %)
14b	50	0.932	0.144	0.856	1.1	0.0686	1460	16.5	33	2240	1.53	95.07	58.0	47.1	44
11	50	0.866	0.3	0.7	1.1	0.143	700	17.0	34	2200	3.14	97.82	58.9	18.4	40
6	15	0.352	0.6	0.4	1.1	0.286	350	20.5	41	1830	5.23	97.63	37.2	8.7	40
5	30	0.569	0.6	0.4	1.1	0.286	350	20.5	41	1830	5.23	93.67	47.3	6.7	45
4	50	0.755	0.6	0.4	1.1	0.286	350	20.5	41	1830	5.23	94.52	54.3	5.6	49
15	9	0.147	1.0	0	1.1	0.476	210	19.5	39	1915	9.13	89.56	16.8	10.7	21
10	23	0.341	1.0	0	1.1	0.476	210	19.5	39	1915	9.13	95.8	34.8	3.8	38
9	37.5	0.509	1.0	0	1.1	0.476	210	19.5	39	1915	9.13	94.43	43.6	2.4	46
8	50	0.633	1.0	0	1.1	0.476	210	19.5	39	1915	9.13	95.0	48.7	2.4	46

[a] MA, maleic anhydride; AA, adipic acid; BD, 1,4-butylene glycol.

TABLE 2. Examination of Funke's Results[a]

Resin			Polyester									Cured resin			
	Styrene		Mole ratio												
No.	Wt%	Mole fraction	MA	AA	BD	Equivalent of double bond/100 g	$\overline{M}_0$	Acid No.	Hydroxyl No.	$\overline{M}_n$	$\bar{x}$	C_S (mole %)	C_F (mole %)	W (mole %)	q (mole %)
4a	50	0.75	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	89	62	3.2	63
4e	50	0.75	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	99	61	4.2	58
4b	50	0.75	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	92	59	5.5	52
5a	30	0.57	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	80	51	5.1	53
5e	30	0.57	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	98	55	4.7	55
5b	30	0.57	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	90	53	6.3	48
6a	22.5	0.47	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	73	11	55.5	8
6e	22.5	0.47	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	98	43	6.9	46
6b	22.5	0.47	0.6	0.4	1.1	0.320	312	25	50	1495	4.8	89	41	8.1	42

[a] MA, maleic anhydride; AA, adipic acid; BD, 1,4-butylene glycol.

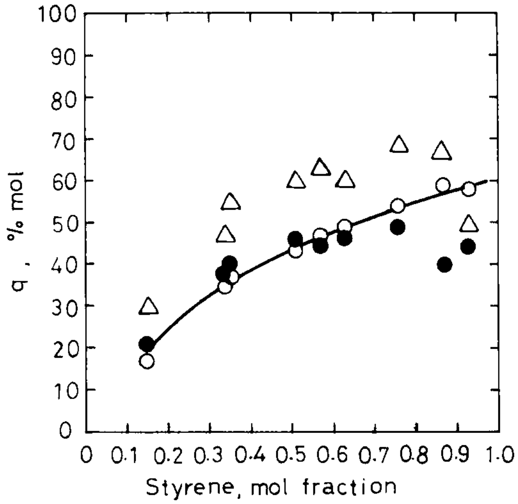

FIG. 5. Examination of Funke's results [1]. (○) Funke's results; (●) Examination of Funke's data by the present equations; and (△) Examination of Funke's data by Shito [10].

compositions were determined by IR spectrum, gas chromatography, and hydrogenation procedure. The equivalent double bond per 100 g of polyester was determined by a hydrogenation procedure using palladium-carbon catalyst.

Conventionally the fumarate double bond in unsaturated polyester resin has been determined by polarographic procedures [11-13] after the hydrolysis of unsaturated polyesters. However, it is reported that fumarate double bond is lost during homogeneous alkaline hydorolysis [14]. Therefore, we have developed a hydrogenation procedure to determine the fumarate double bond of unsaturated polyester resin in the presence of palladium-carbon and a proper solvent without hydrolysis or pre-treatment of the resin.

The apparatus for the determination of fumarate double bond is shown in Fig. 6. The reaction vessel is a 50-ml flask connecting to the gas burette. Both the reaction vessel and the gas burette were kept at a constant 25 ± 0.1°C by the circulation of the water regulated by a thermostat, Coolnics. Diethyl fumarate was utilized as a low molecular weight model compound for unsaturated polyesters. The purity was found to be 99.3% by gas chromatography.

A Bisphenol-type unsaturated polyester resin was used as an unsaturated polyester. The resin is a propoxylated (2.2) bisphenol A

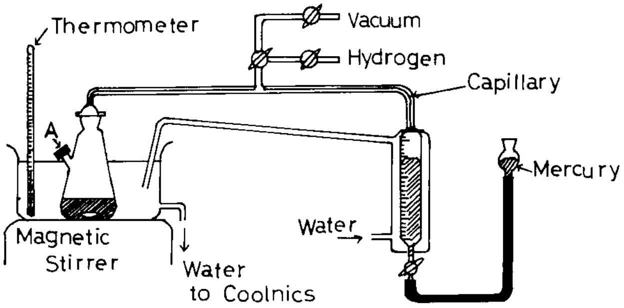

FIG. 6. The apparatus for determination of double bond by hydrogenation.

fumarate having an acid number of 14 and a double bond calculation (equiv/100 g) of 0.224. Palladium-carbon catalyst (60 ± 5 mg) was weighed into the flask and 25 ml of solvent was added. The magnetic stirrer was started and the whole system was purged with hydrogen which was allowed to absorb onto the catalyst for 1 hr. Two milliliters of the sample solution was injected through the gasket (A) by the syringe while the stirrer was stopped. The reaction was started by stirring and continued until the decrease of the volume of hydrogen was levelled off.

The equivalent hydrogen reacted with fumarate double bond, A, was calculated by

$$A = \frac{273(760 - P)a}{T \times 760 \times 22{,}400} \tag{6}$$

where p is the vapor pressure of the solvent in mm Hg at T, a is the volume of hydrogen reacted, and T is the absolute temperature of the circulating water in °K.

M is the concentration of the sample in weight % and G is the weight of the sample injected in g. Then the net weight of the sample, B, is expressed by

$$B = MG/100 \tag{7}$$

The equivalent fumarate double bond per 100 g sample, E, is given by

$$E = \frac{A}{B} \times 100 \tag{8}$$

TABLE 3. Hydrogenation of Diethyl Fumarate

Expt No.	Solvent	Diethyl fumarate		Palladium-carbon (mg)	Reaction time (min)	Hydrogen reacted		Double bond (equiv/100)		Conversion %
		mg	equiv × 10			ml (0°C, 1 atm)	equiv × 10	Calc	Found	
1	Benzene	29.3	1.90	61.3	40	3.75	1.67	0.581	0.573	98.2
2	Ethylene dichloride	40.4	2.35	62.0	60	5.13	2.29	0.581	0.567	97.4
3	Chloroform	38.8	2.25	60.7	60	4.62	2.06	0.581	0.531	91.6
4	Acetone	29.4	1.71	58.2	40	3.18	1.42	0.581	0.483	83.0
5	Dimethyl formamide	26.6	1.54	59.4	50	3.74	1.67	0.581	0.628	108.4
6	Benzene-acetone (1:1)	27.3	1.59	60.3	60	3.47	1.55	0.581	0.568	97.5
7	Benzene-acetone (1:1)	35.4	2.06	61.0	60	4.42	1.97	0.581	0.556	95.6
8	Benzene-acetone (1:1)	33.9	1.97 60.9	60.9	60	4.28	1.91	0.581	0.556	97.0

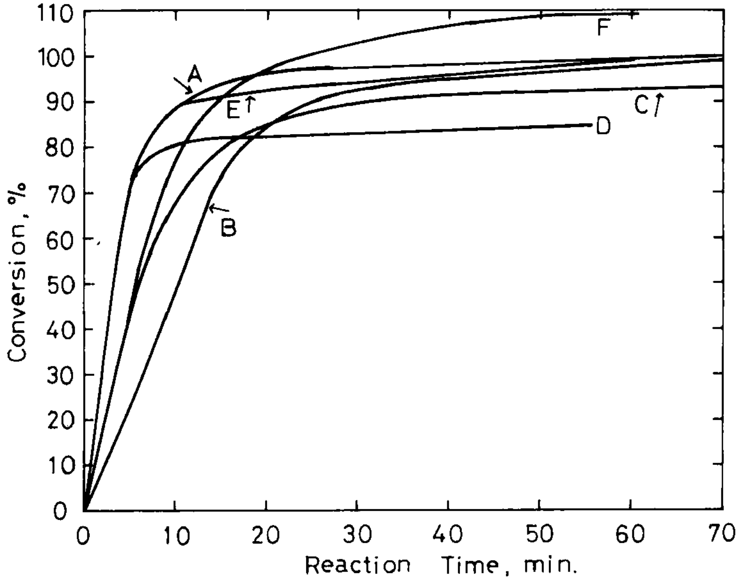

FIG. 7. Hydrogenation of diethyl fumarate. The effect of solvents on the convension vs time curve. (A) Benzene. (B) Ethylene dichloride. (C) Chloroform. (D) Acetone. (E) Benzene-acetone (1:1) mixture. (F) Diethyl formamide.

The experimental results of hydrogenation are as follows. The effect of solvent was first examined in the hydrogenation of diethyl fumarate. The results are summarized in Table 3 and Fig. 7. The initial rate in acetone or benzene is higher than that in ethylene dichloride. Dimethylformamide gives extraordinarily higher conversion than 100%, and acetone gives low conversion after 70 min even though it has a relatively higher initial rate. Incidentally, a benzene-acetone (1:1) mixture was used and the same conversion vs time curve was obtained for all solvents: benzene-acetone (1:1) mixture, benzene, and ethylene dichloride. The ultimate conversion after 60 min approached 97%. A good reproducibility was also obtained in benzene-acetone mixture solvent.

In the hydrogenation of a Bisphenol-type polyester resin, benzene, a benzene-acetone mixture, and ethylene dichloride, which showed satisfactory hydrogenation, were also examined. The results are shown in Table 4. As shown in Fig. 8, a benzene-acetone (1:1) mixture gives a higher initial rate and an ultimate conversion of 97.2%. The reproducibility is also good for the polymer. The rate of hydrogenation for the polyester

TABLE 4. Hydrogenation of Polyester

Expt No.	Solvent	Polyester		Palladium-carbon	Reaction time	Hydrogen reacted		Double bond (equiv/100 g)		Conversion
		mg	equiv × 10	(mg)	(min)	ml 0°C, 1 atm)	equiv × 10	Calc	Found	(%)
9	Benzene	92.8	2.08	60.6	60	4.54	2.03	0.224	0.219	97.6
10	Ethylene dichloride	92.9	2.08	61.0	60	4.13	1.84	0.224	0.198	88.5
11	Benzene-acetone (1:1)	79.5	1.78	61.2	50	3.88	1.73	0.224	0.218	97.2
12	Benzene-acetone (1:1)	82.2	1.84	61.0	60	4.07	1.82	0.224	0.221	98.9
13	Benzene-acetone (1:1)	80.9	1.81	60.6	60	3.96	1.77	0.224	0.219	97.7

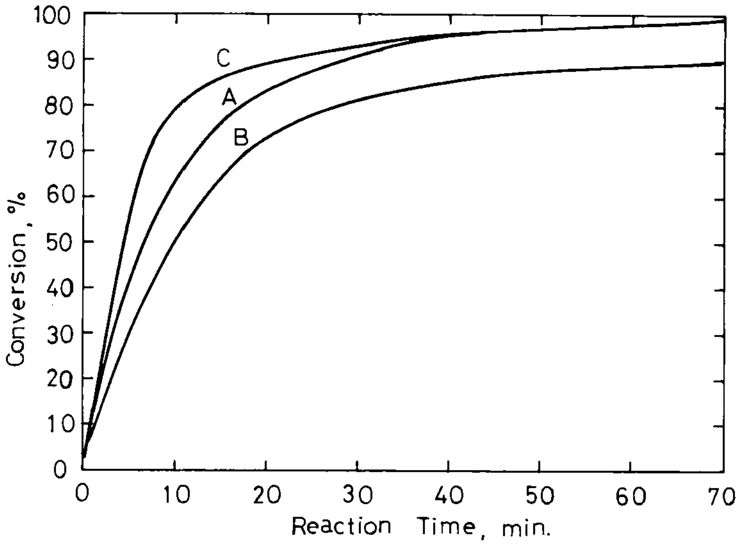

FIG. 8. Hydrogenation of polyester resin. The effect of solvents on the conversion vs time curve. (A) Benzene, (B) Ethylene dichloride. (C) Benzene-acetone (1:1) mixture.

is a little slower than that for dimethyl fumarate, but the conversions reach a maximum after 60 min. The initial rate and the ultimate conversion after 60 min for both the polyester and the diethyl fumarate are shown in Table 5.

There is no essential difference between the polyester and diethyl fumarate in the initial rate and the ultimate conversion in benzene-acetone solvent. In benzene the initial rate for the polyester is remarkably slower than that for diethyl fumarate, but the ultimate conversion for both the polyester and diethyl fumarate is at the same level. It is characteristic that the ultimate conversion for the polyester is lower than that for diethyl fumarate in ethylene dichloride. These variations in the hydrogenation behavior may be due to the solubility of the polyester or diethyl fumarate and their hydrogenated products in each solvent. Essentially, the reactivity of the fumarate double bond in the polyester seemed to be almost the same as that of the double bond of low molecular weight diethyl fumarate. This fact coincide with the principles of equal reactivity of the functional group in a polymer as proposed by Flory [9].

Based on the above experiment, the fumarate double bond of commercial unsaturated polyesters which have been used in this study were determined by the optimized hydrogenation as follows:

TABLE 5. Comparison of the Initial Rate and The Ultimate Conversion

	Diethyl fumarate		Polyester	
Solvent	Initial rate (% conversion/min)	Ultimate conversion (%)	Initial rate (% conversion/min)	Ultimate conversion (%)
Benzene	0.89	98.2	0.62	97.6
Benzene-acetone (1:1)	0.89	97.5	0.84	97.2
Etylene dichloride	0.50	97.4	0.48	88.5

catalyst, 60 ± 5 mg of palladium-carbon; solvent, 25 ml of benzene-acetone (1:1) mixture; polyester sampled, 80 ± 20 mg; and reaction time, 60 min.

$\overline{M}_0$ for commercial polyester resins is calculated from the double bond concentration:

$$\overline{M}_0 = \frac{100}{\text{double bond (equiv/100 g)}} \tag{9}$$

Their chemical characteristics are shown in Table 6. The molecular weight distribution of the polyester used was found to agree with Flory's most probable distribution by the measurement of gel permeation chromatography. For example, a Bisphenol-type resin in Table 6 has a number-average molecular weight ($\overline{M}_n$) of 2340 and a weight-average molecular weight ($\overline{M}_w$) of 4910. The ratio of $\overline{M}_w/\overline{M}_n$ is 2.1. When $\overline{M}_w/\overline{M}_n$ is 2.0, the distribution follows Flory's most probable distribution.

Determination of Residua' Styrene Content and Unreacted Polyester Resin in the Cured Resin

The polyester resin (100 phr) was cast in a cell of 3 mm thickness with 0.1 phr of dimethyl anilin, 0.5 phr of cobalt naphthenate (6.0% active), and 0.7 phr of methyl ethyl ketone peroxide (60% active). The resin was allowed to cure at 20°C for 24 hr or postcured at 100°C for 2 hr. The cured resin was rasped with a steel file at slow, steady strokes to prevent overheating. Five grams of raspings was extracted twice with 150 g of chloroform shaken in a funnel for 24 hr at room temperature, and then filtered off. The styrene in the extract solution was determined satisfactorily by ASTM D-1159, bromine index method. The extract solution was then evaporated on a steam bath and dried in vacuo at 100°C. The IR spectrum suggests that the residue consists not only of unsaturated polyester but also of a small amount of polystyrene and other impurities, perhaps the residue of catalyst and cocatalyst, but assuming that the solid in the extract is almost uncrosslinked polyester, the conversion of fumarate double bond, q, can be determined from the relationship between W and q in Fig. 4.

RESULTS AND DISCUSSION

The results for the resin which was cured at 20°C for 24 hr or postcured at 100°C for 2 hr after the room temperature cure of 24 hr are

TABLE 6. Conversion of Styrene and Fumarate Double Bond in Various Unsaturated Polyester Resins[a]

Resin				Polyester							Cured resin				
		Styrene													
No.	Type	wt%	Mole fraction	Composition	Equivalent of double bond/100 g	$\overline{M}_0$	Acid No.	Hydroxyl No.	$\overline{M}_n$	$\overline{x}$	RT cured or post cured	Barcol hardness	C_s (mole %)	W (mole %)	q (mole %)
1	Bisphenol	50.6	0.82	FA/PO(2)BPA	0.219	456	11.7	36.2	2340	5.1	RT cured	10.3	80.7	3.14	61
2	Bisphenol	50.6	0.82	FA/PO(2)BPA	0.219	456	11.7	36.7	2340	5.1	Post cured	42.3	98.5	3.22	61
3	Iso, high HDT	38.8	0.58	IPA/FA/PG	0.450	222	26.3	62.6	1260	5.6	RT cured	19.3	81.5	5.87	45
4	Iso, high HDT	38.8	0.58	IPA/FA/PG	0.450	222	26.3	62.6	1260	5.6	Post cured	52.3	99.2	3.71	55
5	G	30.6	0.69	PA/MA/PG	0.189	529	56.3	10.7	1670	3.2	RT cured	25.7	88.9	17.15	26
6	G	30.6	0.69	PA/MA/PG	0.189	529	56.3	10.7	1670	3.2	Post cured	50.0	99.2	11.15	42
7	Iso	39.2	0.79	IPA/MA/PG	0.164	610	14.1	21.6	3140	5.2	RT cured	13.7	78.4	12.5	32
8	Iso	39.2	0.79	IPA/MA/PG	0.164	610	14.1	21.6	3140	5.2	Post cured	48.7	99.7	7.67	42

[a] HDT, heat distortion temperature; FA, fumaric acid; PO(2)BPA, 2,2-propoxylated bisphenol A; BPA, bisphenol A; IPA, isophthalic acid; PG, propylene glycol; PA, phthalic anhydride; MA, maleic anyhydride; RT, room temperature.

shown in Table 6. Several important facts are found in the results of Table 6. The conversion of fumarate double bond q is relatively higher for Bisphenol-type resin than for G-type or Iso-type resins. As shown by Funke et al. [3], the results in this experiment show that the polyester prepared from maleic anhydride gives lower conversion value of fumarate double bond than the polyester from fumaric acid. In the case of Bisphenol-type resin, there is no essential difference in the values of conversion of fumarate double bond between room temperature-cure and postcure. On the other hand, the conversion of fumarate double bond increased remarkably by postcure in the case of G-type and Iso-type resins. For all polyesters studied in this experiment, the conversion of styrene reached at least 80% by room temperature cure and was developed to 98-99% by postcure. Styrene was copolymerized completely by postcure; however, the ultimate conversion of fumarate double bond for all polyesters was lower than expected.

In the case of Bisphenol-type resin, a few behavior characteristic which differ from G-type and Iso-type resins in the polymerization process. The reaction between fumarate double bond and styrene has been finished by room temperature cure although the Barcol hardness is still 10.3 and the styrene unreacted is 19.3%. At the next stage of postcuring, styrene was copolymerized completely without an increase of the conversion of fumarate double bond q. These facts suggest that the styrene polymerized at the postcuring stage adds to a styrene radical of the polyester-styrene copolymer rather than to a fumarate double bond.

Table 7 shows the Barcol hardness development, the conversion of styrene C_S, and the conversion of fumarate double bond q with the cure time at 20°C in the polymerization of a Bisphenol-type resin. Figure 9 shows the Barcol hardness development with time, Fig. 10 shows the increase of the conversion of styrene C_S and the conversion of fumarate double bond q with time, and Fig. 11 shows the plot of Barcol hardness vs the conversion of styrene C_S. In these results we have observed the interesting facts that the conversion of styrene C_S increases with an increase of the Barcol hardness but that the conversion of fumarate double bond q levels off with the Barcol hardness. The conversion of styrene can be estimated for the specified polyesters from the curve of Barcol hardness vs the conversion of styrene C_S.

CONCLUSIONS

The conversion of styrene and fumarate double bond in the copolymerization of unsaturated polyesters and styrene can be determined

TABLE 7. Barcol Hardness Development, Conversion of Styrene and Fumarate Double Bond with Cure Time in Bisphenol-type Resin

Cure time (days at 20°C)	Barcol hardness	C_S (mole %)	W (mole %)	q (mole %)
1	7.0	75.24	3.36	60
3	14.7	78.68	3.22	61
4	16.3	80.24	3.08	62
13	22.2	83.94	3.26	61
65	33.3	88.82	3.38	60
Postcured[a]	44.7	98.72	3.20	61

[a] After 1 day the resin was postcured at 100°C for 2 hr.

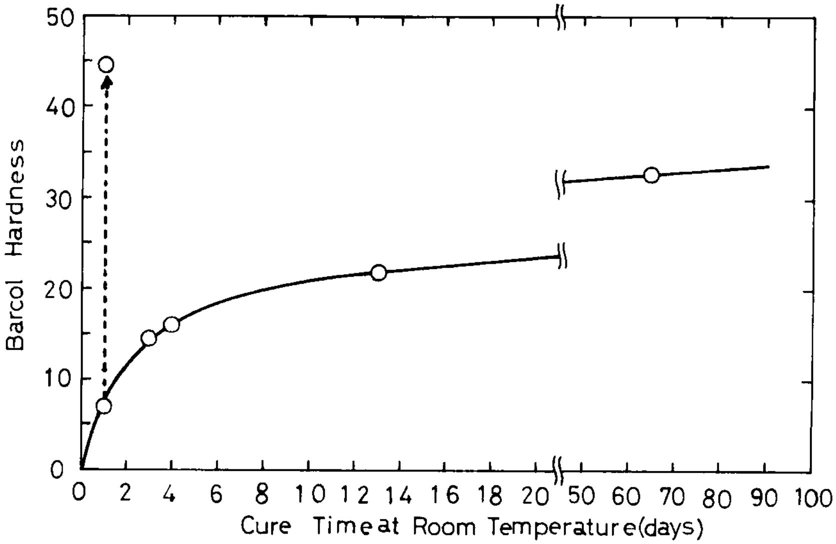

FIG. 9. The relationship between Barcol hardness and cure time.

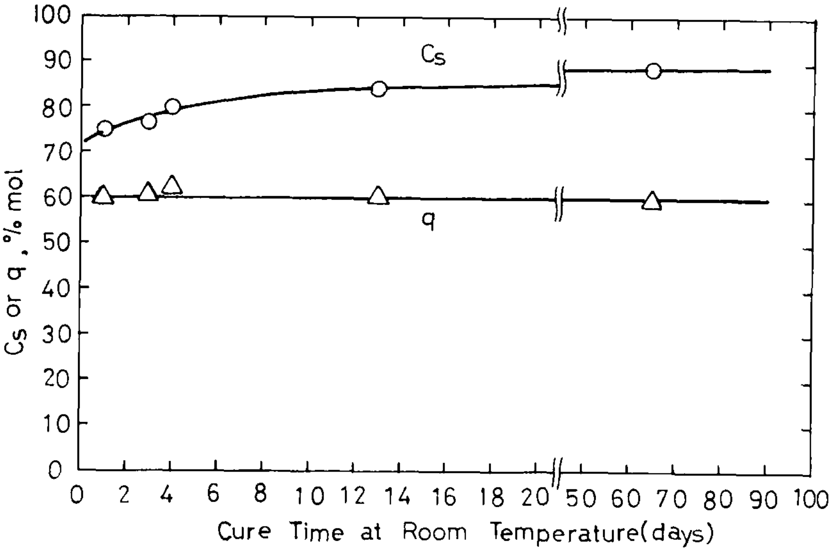

FIG. 10. The relationship between C_S or q and cure time.

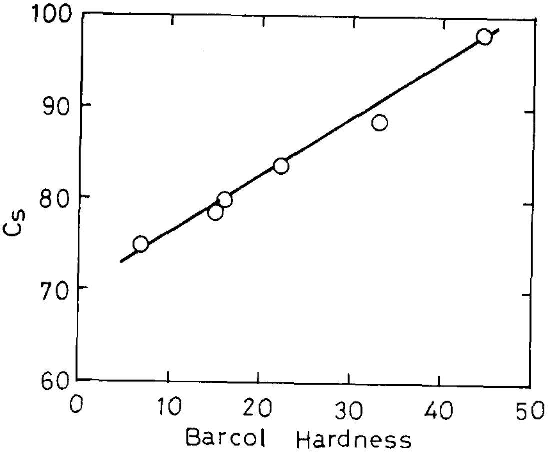

FIG. 11. The relationship between C_S and Barcol hardness.

by the chloroform extraction of the soluble component in the cured resin. The conversion of styrene can be easily analyzed by the titration of the extracted solution using ASDM-1159, bromine index method. The conversion of fumarate double bond can be calculated from the solid polyester resin in the extracted solution by using theoretical equations derived from the basic theory of Flory.

The conversion of styrene is at best 80% in room temperature cure but reaches almost 100% when the resin is postcured. The conversion of fumarate double bond is greatly influenced by the type of resin. The conversion of styrene can be estimated for the specific polymers by the measurement of the Barcol hardness if we have the relationship between the Barcol hardness and the conversion of styrene.

ACKNOWLEDGMENTS

The author wishes to express his thanks to Mr. Jun-ichi Furukawa for experimental assistance. Appreciation is also extended to Professor T. Saegusa of Kyoto University for his helpful discussion.

REFERENCES

[1] W. Funke, W. Gabhardt, H. Roth, and K. Hamann, Makromol. Chem., 28, 17 (1958).

[2] W. Funke, H. Roth, and K. Hamann, Kunststoffe, 51, 75 (1961).

[3] W. Funke and H. Janssen, Makromol. Chem., 50, 188 (1961).

[4] W. Funke and K. Hamann, Mod. Plast., 39, 147, 148, 150, 226 (1962).

[5] K. Hamann, W. Funke, and H. Gilch, Angew. Chem., 71, 596 (1959).

[6] N. A. Ghanem, Makromol. Chem., 36, 109 (1960).

[7] M. Bohdanecký, J. Mleziva, A. Sternschuss, and Zvonař, Ibid., 47, 201 (1961).

[8] K. Demmler, Kunststoffe, 56, 606 (1966).

[9] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York, 1953.

[10] N. Shito, Nippon Kagaku Zasshi, 82, 1441, 1446 (1961).

[11] P. D. Garn and E. W. Halline, Anal. Chem., 27, 1563 (1955).

[12] E. W. Hobart, Ibid., 26, 1291 (1954).

[13] P. D. Garn and H. M. Giloroy, Ibid., 30, 1663 (1958).

[14] P. Fijolka, J. Lenz, and F. Runge, Makromol. Chem., 26, 61 (1958).

Accepted by editor August 18, 1973
Received for publication September 19, 1973