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Conversion of Fumarate Double Bonds in Unsaturated Polyester Resins in Copolymerization with Styrene

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ABSTRACT

Several varieties of unsaturated polyester resins were prepared to investigate the effect of chemical structure and molecular weight and the initial mole fraction of styrene on the conversion of fumarate double bond in the copolymerization with styrene.

The conversion of the fumarate double bond was calculated from the soluble portion of polyester resin, according to the theoretical equations which were proposed in a previous paper. Conversion first increased with increasing initial mole fraction of styrene. At an initial mole fraction of styrene higher than 0.6-0.7, however, the conversion of fumarate double bond decreased.

Styrene homopolymer was separated from the soluble material by elution chromatography on a silica gel-packed

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column. The purity of polyester component in the soluble part of the polyester resin was determined by infrared spectroscopy and by the saponification number. The conversion of fumarate double bond was calibrated by using corrected values of the soluble part of polyester resin.

The chemical structure and the molecular weight of unsaturated polyester resins also affect the conversion of fumarate double bond. In Bisphenol-type resins, the conversion of fumarate double bond increased with the extension of polyoxypropylene unit attached to Bisphenol A, and the increase of the molecular weight of primary polyester resin was unfavorable for the conversion of fumarate double bond. In a series of propylene glycol fumarate resins, the adipic acid-modified resin gave a higher conversion of fumarate double bond than the isophthalic acid-modified resin and the phthalic acid-modified resin. The polyester resin prepared from chlorendic anhydride gave the lowest conversion of fumarate double bonds among the polyester resins investigated in the present paper.

The extent of conversion of fumarate double bond may be restricted by the properties of the network such as rigidity, the crosslinking density, and steric hindrance of groups like chlorine.

INTRODUCTION

The mechanical, electrical, and chemical properties of polyester resins are related to the degree of cure of the resin. Many investigators have tried to determine the degree of cure by means of physical and chemical methods. The degree of cure has been expressed by the conversion of styrene and fumarate double bonds. The conversion of styrene can be easily determined by solvent extraction of the powdered resins, with subsequent analysis of styrene by using either ASTM Method D-1159, the bromine index method, or gas chromatography. On the other hand, the conversion of fumarate double bond is difficult to determine. Funke et al. [1-5] and other investigators [6-8] have used the alkaline hydrolysis method for the determination of the conversion of fumarate double bond. They hydrolyzed the cured polyester resin by alkali and analyzed the residue by elemental analysis and infrared spectroscopy.

Previously, one of the present authors [9] presented a paper on the determination of the conversion of fumarate double bonds which were crosslinked into three-dimensional polymers. The experiments

were based on the chloroform extraction of the crosslinked resin. The conversion of fumarate double bond was calculated from the soluble portion of polyester resin by using theoretical equations derived from the basic theory of Flory [10].

In the present paper, factors affecting the conversion of fumarate double bonds in unsaturated polyester resins were investigated. Several varieties of unsaturated polyester resins including Bisphenol-type, iso-type, G-type, and Het acid-type resins were prepared with varying chemical compositions, molecular weight of the primary polyester resin, and the initial concentration of styrene.

EXPERIMENTAL

All unsaturated polyester resins were prepared in a four-necked, round-bottomed, 5-liter flask kettle equipped with a stirrer, nitrogen gas inlet, thermometer, and distillation head. When glycols of relatively low boiling point such as propylene glycol and neopentyl glycol were esterified, a distillation head packed with stainless steel mesh packings was used to enhance the efficiency in separation of the water from the glycols. Esterification was usually carried out in one step, but a two-step process was used for iso-type resin. Reaction mixtures including 400 ppm of hydroquinone as inhibitor were charged into the kettle and heated by a mantle with a stream of nitrogen gas during the esterification. The reaction was carried out at the temperatures from 140 to 210°C to appropriate molecular weight. Several varieties of the resins were prepared.

Bisphenol-Type Resin

The standard resin in Bisphenol-type resin is a condensate of propoxylated (2.2 mole) Bisphenol A and fumaric acid. The resins having the different degrees of esterification were prepared by changing the reaction time. To change the average molecular weight between the two fumarate units, the resin was modified by extending the propoxylate unit adducted to Bisphenol A, and incorporating neopentyl glycol, propylene glycol, hydrogenated Bisphenol A and β -hydroxyethyl terephthalate as a glycol component, and succinic acid and adipic acid as a dibasic acid component.

G-Type, Iso-Type, and Het Acid-Type Resins

Propylene glycol fumarate is the standard resin in G-type resins. The only modifications made were in the acid components, different

amounts of phthalic anhydride and adipic acid being used to prepare the resin having the various average molecular weight between the two fumarate units. An iso-type resin and a Het acid-type resin were prepared by using isophthalic acid and Het-acid (chlorendic anhydride), respectively.

The unsaturated polyester resins prepared were characterized by acid number, hydroxyl number and saponification number. The equivalents of fumarate double bonds and the average molecular weight between the two fumarate units, \bar{M}_0 , were calculated from the composition charged. The number-average molecular weight for the polyesters, \bar{M}_n , was determined by endgroup analysis, acid number, and hydroxyl number. The resins thus obtained were dissolved in styrene at an appropriate concentration at room temperature. Polyester-styrene solutions were cured with a catalyst mixture of 0.1% dimethylaniline, 0.5% cobalt naphthenate (as a 6% solution) and 1% methyl ethyl ketone peroxide (as a 55% solution). The catalyzed resin solution was poured into a mold consisting of two plates of glass which were covered with polyester film and separated by a 4 mm poly(vinyl chloride) spacer, and the resin was allowed to cure at room temperature for 24 hr. The castings were then placed in an oven at 100° C for 2 hr for completion of the cure.

The cured resins were rasped with steel file with slow, steady strokes to prevent overheating, and 10 g of powdered resin was extracted three times with 300 g of chloroform. The resin-solvent mixture was filtered off for each extraction. The extract solution was analyzed for unreacted styrene which was satisfactorily determined by gas chromatography method. The solutions were then evaporated on a steam bath and dried in vacuo at 100° C. The resins extracted from the cured resin were subjected to further analysis by elution chromatography of silica gel-packed column, acid number, hydroxyl number, saponification number, gel permeation chromatography, and infrared spectroscopy.

RESULTS AND DISCUSSION

The results for the various polyester resins are summarized in Tables 1-3. The initial concentration of styrene in the polyester resin solution is 50 ± 0.5 wt % for all resins, so the initial mole fraction of styrene, f_{S_0} , for each polyester resins varies with the average molecular weight between two fumarate units, \bar{M}_0 .

The conversion of styrene C_S is above 90% for all resins. The

TABLE 1. Chemical Characteristics of Various Polyester Resins

Expt. no.	Resin no.	Type	Unsaturated polyester resin						Styrene			
			Composition (mole ratio) ^a	Fumarate double bond (eq/100 g)	\bar{M}_0	Acid no.	Hydroxyl no.	Saponification no.	\bar{M}_n	\bar{x}	f_{So} (mole fraction)	wt %
1	B(2)-1	Bisphenol	B(2)/FA =1/1	0.219	456	4.4	23.4	248.7	4040	8.9	49.7	0.812
2	B(2)-2	Bisphenol	B(2)/FA =1/1	0.219	456	7.8	26.2	243.8	3300	7.2	50.0	0.814
3	B(2)-4	Bisphenol	B(2)/FA =1/1	0.219	456	11.9	28.3	250.0	2794	6.1	50.0	0.814
4	B(2)-5	Bisphenol	B(2)/FA =1/1	0.219	456	11.9	30.1	242.9	2672	5.9	50.0	0.814
5	B(2)-6	Bisphenol	B(2)/FA =1/1	0.219	456	25.4	28.6	259.1	2078	4.6	50.0	0.814
6	B(2)-7	Bisphenol	B(2)/FA =1/1	0.219	456	30.8	33.7	255.4	1740	3.8	50.0	0.814
7	B(2)-8	Bisphenol	B(2)/FA =1/1	0.219	456	19.0	60.1	227.1	1419	3.1	49.8	0.813
8	B(2)-9	Bisphenol	B(2)/FA =1/1	0.219	456	22.8	81.9	213.3	1072	2.4	49.7	0.812
9	B(5)	Bisphenol	B(5)/FA =1/1	0.174	586	22.4	26.4	169.7	2300	3.9	50.2	0.850
10	B(9)	Bisphenol	B(9)/FA =1/1	0.214	809	21.5	31.8	136.2	2105	2.6	50.0	0.886
11	B(15)	Bisphenol	B(15)/FA-1/1	0.086	1158	12.9	41.1	90.6	2078	1.8	50.0	0.918
12	BM-NG-1	Bisphenol	B(2)/NPG/FA =1/1/2	0.321	312	10.5	62.7	316.0	1533	4.9	50.1	0.750
13	BM-PG-2	Bisphenol	B(2)/PG/FA =1/1/2	0.399	295	22.5	30.8	371.4	2105	7.1	49.9	0.738
14	BM-MB-1	Bisphenol	B(2)/HBPA/FA =1/1/2	0.264	378	28.2	31.8	285.5	1870	5.0	49.5	0.781

(continued)

TABLE I (continued)

Expt. no.	Resin no.	Type	Composition (mole ratio) ^a	Unsaturated polyester resin							Styrene	
				Fumarate double bond (eq/100 g)	\bar{M}_0	Acid no.	Hydroxy no.	Saponification no.	\bar{M}_n	\bar{x}^c	wt %	f_{S_0} (mole fraction)
15	BM-HETPA	Bisphenol	B(2)/HETPA/FA =1/1/2	0.260	384	26.5	30.1	415.9	2400	5.2	50.1	0.787
16	BM-SA-1	Bisphenol	B(2)/SA/FA =3/1/2	0.151	661	20.6	33.2	250.3	2086	3.2	49.7	0.863
17	BM-SA-2	Bisphenol	B(2)/SA/FA =2/1/1	0.116	862	21.9	31.3	249.7	2109	2.5	49.9	0.892
18	BM-AA-1	Bisphenol	B(2)/AA/FA =3/1/2	0.148	675	12.8	29.9	240.2	2628	3.9	50.2	0.867
19	BM-AA-2	Bisphenol	B(2)/AA/FA =2/1/1	0.110	911	20.3	31.8	239.7	2154	2.4	50.0	0.897
20	IPA	Iso	PG/IPA/FA =3.3/2/1	0.169	591	24.7	39.9	575.7	1740	2.9	50.4	0.853
21	G-1	G	PG/FA=1.05/1	0.641	156	22.8	38.5	674.8	1831	11.7	50.2	0.601
22	G-2	G	PG/PA/FA =1.47/0.33/1.0	0.415	241	17.2	44.1	628.6	1831	7.6	50.1	0.699
23	G-3	G	PB/PA/FA =3.3/1/2	0.369	271	25.4	49.5	608.8	1498	5.5	49.7	0.720
24	G-4	G	PG/PA/FA =2.2/1/1	0.265	378	19.3	45.9	589.4	1721	4.6	49.8	0.783
25	G-5	G	PG/PA/FA =3.3/2/1	0.169	591	16.7	42.6	565.0	1892	3.2	50.0	0.850
26	G-7	G	PG/AA/FA =3.3/2/1	0.181	552	21.7	34.2	613.7	2007	3.6	50.0	0.841
27	G-8	G	PG/AA/FA =4.4/3/1	0.134	746	24.3	34.4	620.0	1910	2.6	50.0	0.877
28	G-9	G	PG/AA/FA =5.5/4/1	0.106	940	23.0	35.1	598.0	1931	2.1	50.0	0.900

29	HETA	HET-Acid	NPG/HETA/FA = 1.5/0.46/1.0	0.246	406 =	29.1	25.6	406.6	2051	5.1	50.0	0.796
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^a B(2), 2,2-propoxylated Bisphenol A; FA, fumaric acid; B(5), 5-propoxylated Bisphenol A; B(9), 9-propoxylated Bisphenol A; B(15), 15-propoxylated Bisphenol A; NPG, neopentyl glycol; PG, propylene glycol; HBP, hydrogenated bisphenol A; HETPA, β -hydroxyethyl terephthalate; SA, succinic acid; AA, adipic acid; IPA, isophthalic acid; PA, phthalic anhydride; HETA, hexachlorendic anhydride.

$$b \bar{M}_n = 56.108 \times 2000 / (\text{acid no.} + \text{hydroxyl no.})$$

$$c \bar{x} = \bar{M}_I / \bar{M}_0, \text{ where } \bar{M}_0 \text{ is the number-average molecular weight between two fumarate units.}$$

TABLE 2. Results of Chloroform Extraction of Various Cured Polyester

Expt. no.	Analysis of polyester resins extracted										Purity of polyester component (
	CS (mole %)	W ₀ (mole %)	q ₀ (mole %)	Acid. no.	Hydroxyl no.	Saponification no.	MSOL (from EGA)	MSOL (from GPC)	By IR By			
									IR	By		
1	98.9	3.76	39	20.2	87.1	145	1046	888	59	58.		
2	99.1	3.48	47	13.3	62.2	142	1486	725	60	58.		
3	98.0	2.50	59	13.8	113.0	144	885	1284	51	58.		
4	98.0	3.64	53	17.1	106.1	126	911	1050	62	52.		
5	98.5	2.98	66	43.0	119.8	176	689	538	72	68.		
6	97.9	4.49	65	32.5	144.3	204	635	635	66	80.		
7	97.9	7.85	60	15.2	176.6	119	585	779	53	52.		
8	99.9	12.70	58	10.5	193.8	92.5	549	839	51	43.		
9	99.6	5.76	58	31.3	86.7	104.8	951	1411	46	61.		
10	100	8.22	66	19.2	92.6	101.1	1004	2046	60	74.		
11	100	12.42	70	18.6	83.2	90.3	1102	1175	86	99.		
12	97.0	5.49	51	14.0	207.1	137.8	508	560	45	43.		
13	97.5	2.04	58	—	—	242.2	—	551	71	65.		
14	97.8	4.04	57	33.3	148.2	178.4	618	655	78	62.		
15	95.7	4.77	52	49.0	76.1	337.5	897	786	77	81.		

CONVERSION OF FUMARATE DOUBLE BONDS

16	100	10.20	53	13.1	58.6	147.6	1565	2868	36	59.0	3.67	74	6.01	65
17	100	17.05	49	14.4	44.3	202.3	1912	3013	54	81.0	9.21	64	13.81	54
18	100	10.32	45	10.3	56.0	139.1	1693	2010	47	57.9	4.85	62	5.98	57
19	100	19.40	47	11.9	35.6	171.5	2362	3318	53	71.5	10.28	63	13.88	56
20	100	13.60	49	34.9	51.3	452.1	1302	944	62	78.5	8.43	61	10.68	55
21	96.4	2.33	39	-	-	373	-	414	53	55.3	1.23	50	1.29	49
22	96.5	3.49	45	-	-	454	-	-	77	72.3	2.69	50	2.52	51
23	98.7	5.61	46	89.7	76.5	425	675	700	87	69.8	4.88	49	3.92	54
24	100	8.82	43	75.9	89.2	443	680	765	83	75.2	7.32	47	6.63	49
25	100	15.24	43	46.3	56.1	476	1096	650	61	84.3	9.30	55	12.85	47
26	100	7.53	55	11.5	125.7	503	818	800	82	82.0	6.18	60	6.18	60
27	100	11.74	57	50.9	61.8	462	996	1135	81	74.6	9.51	62	8.76	64
28	100	15.06	59	48.4	67.6	523	967	750	95	87.6	14.31	60	13.18	62
29	99.8	12.36	33	45.9	39.7	337.5	1311	1250	79	83.0	9.76	37	10.26	36

TABLE 3. Effects of f_{S_0} on the Chloroform Extraction of Various Cured Polyester Resins

Expt. no.	Resin no.	Styrene		CS (mole %)	W_0 (mole %)	q_0 (mole %)	\bar{M}_{SOL} (from EGA)	\bar{M}_{SOL} (from GPC)	Purity of polyester component (%)		q_{IR} (mole %)	W_{SN} (mole %)	q_{SN} (mole %)	
		wt %	mole fraction						By IR	By SN				
4-1	B(2)-5	39.1	0.738	98.5	2.99	57	619	500	78	66	2.33	62	1.96	65
4	B(2)-5	50.0	0.814	98.0	3.64	53	911	1050	62	52	2.26	63	1.89	66
4-2	B(2)-5	60.2	0.869	99.4	7.76	38	1626	1811	28	30	2.17	63	2.30	62
8-1	B(2)-9	29.7	0.649	97.9	12.02	60	467	430	92	83	11.06	62	9.96	64
8	B(2)-9	49.7	0.812	99.9	12.70	58	549	839	51	43	6.48	73	5.51	76
8-2	B(2)-9	70.0	0.911	99.6	34.27	30	1237	4946	26	27	8.91	67	9.25	66
10-1	B(9)	5.0	0.290	90.4	32.43	30	948	1197	100	98	32.43	30	31.78	30
10-2	B(9)	15.0	0.578	100	6.04	72	852	667	97	96	5.86	73	5.77	73
10	B(9)	50.0	0.886	100	8.22	66	1004	2046	60	74	4.93	76	6.10	72
11-1	B(15)	5.0	0.369	100	17.87	61	1326	984	100	99	12.87	61	17.69	61
11-2	B(15)	15.0	0.662	100	9.89	75	918	1009	96	99	9.47	76	9.79	75
11-3	B(15)	30.7	0.831	100	10.78	73	1124	1100	88	99	9.49	76	10.67	73
11	B(15)	50.0	0.918	100	12.42	70	1102	1175	86	100	10.68	73	12.17	70
11-4	B(15)	68.0	0.961	100	12.92	69	1069	1200	83	90	10.72	73	11.59	71
20-1	IPA	28.9	0.697	100	11.28	54	846	600	90	100	10.15	56	11.28	54
20	IPA	50.4	0.853	100	13.60	49	1302	944	62	79	8.43	61	10.68	55
20-2	IPA	70.0	0.930	99.9	20.00	39	1638	3607	43	48	8.60	60	9.61	58

CONVERSION OF FUMARATE DOUBLE BONDS

23-1	G-3	29.7	0.524	98.9	7.25	41	605	650	90	94	6.53	43	6.80	42
23	G-3	49.7	0.720	98.7	5.61	46	675	700	87	70	5.78	49	3.92	54
23-2	G-3	70.0	0.859	100	18.07	23	1954	3473	32	36	5.78	45	6.42	44
26-1	G-7	7.5	0.300	100	22.00	30	1083	750	99	100	21.78	30	22.00	30
26-2	G-7	15.0	0.483	100	6.65	58	699	560	98	92	6.52	59	6.14	60
26-3	G-7	30.2	0.696	100	5.80	61	672	670	98	92	5.68	62	5.34	63
26	G-7	50.0	0.841	100	7.53	55	818	800	82	82	6.18	60	6.18	60
26-4	G-7	69.6	0.924	100	9.90	49	1084	2493	73	61	7.25	56	6.07	60
28-1	G-9	5.0	0.422	100	34.78	34	1251	1277	100	100	34.78	34	34.78	34
28-2	G-9	15.0	0.614	99.6	12.88	63	836	900	98	98	12.62	64	12.63	64
28-3	G-9	30.0	0.795	100	13.25	62	875	751	100	89	13.25	62	11.71	65
28	G-9	50.0	0.900	100	15.06	59	967	750	95	88	14.31	60	13.18	62

conversion of fumarate double bond q_0 was calculated from the soluble part of the cured polyester resin, W_0 , as presented in the previous paper [9]. The soluble part, W , of the polyester resin is given by

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

where q is the conversion of fumarate double bond, x is the number of units in the polyester chain, and W_x is the weight fraction of molecule containing x units.

The values of q_0 apparently vary with the chemical structure and composition of the starting unsaturated polyester resins.

The relationships between f_{S_0} and q_0 are shown in Figs. 1 and 2 for Bisphenol-type resins and for Iso-type and G-type resins, respectively, where the effect of chemical characteristics of the unsaturated polyester resins on q_0 at the same levels of f_{S_0} are exemplified. As f_{S_0} increases, q_0 increases up to $f_{S_0} = 0.6$; the highest q_0 is attained at $f_{S_0} = 0.6 \sim 0.7$. At the levels higher than this region, q_0 decreases. This observation is not in accord with the results by other investigators [1, 2, 6, 7, 8, 11].

Figures 1 and 2 show that the effect of M_0 on q_0 is very distinctive. In comparison, at the region of $f_{S_0} = 0.6 \sim 0.7$ where q_0 reaches its

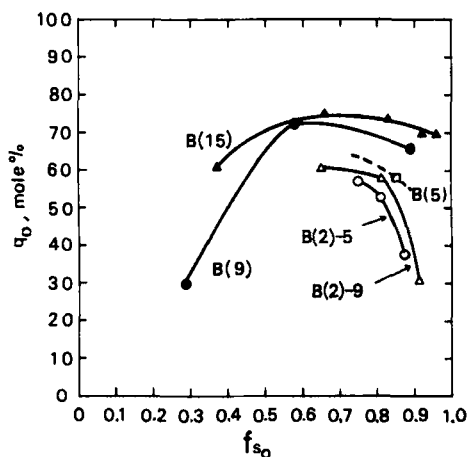


FIG. 1. Relationship between f_{S_0} and q_0 for Bisphenol-type resins.

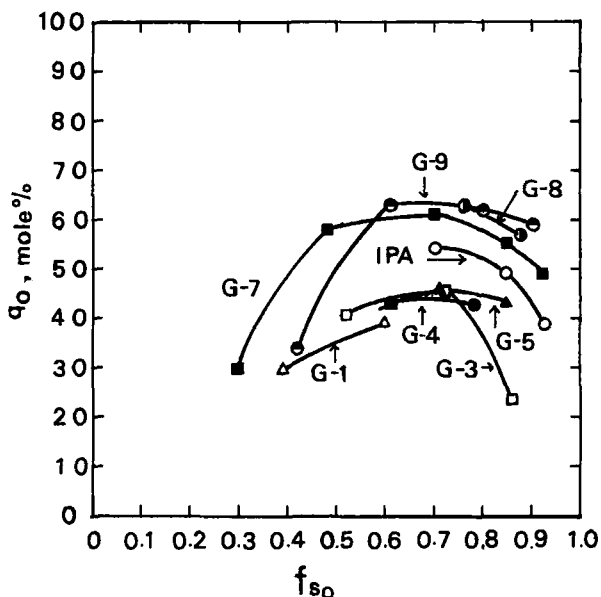


FIG. 2. Relationship between f_{S_0} and q_0 for Iso-type and G-type resins.

peak, the larger the \bar{M}_0 , the higher the q_0 . For instance, \bar{M}_0 for Bisphenol-type resins increased with increasing length of the polyoxypropylene unit attached to Bisphenol A. The increase in \bar{M}_0 enhances the flexibility of the cured resin, which seems to be favorable for raising the conversion of fumarate double bond. The results for G-type and iso-type resins in Fig. 2 show the same relationships between \bar{M}_0 and q_0 as that for Bisphenol-type resins. The type of dibasic acid used as the modifier has a large effect on q_0 . The adipic acid modification gave the highest q_0 , the isophthalic acid modification gave intermediate values of q_0 , and the phthalic acid modification and the unmodified resin having the smallest in \bar{M}_0 gave the lowest q_0 . These results suggest that the network structure of copolymer may affect distinctively the reactivity of fumarate double bonds with styrene.

The acid number and hydroxyl number of the extracted resin were determined. If the extracted polymer consists purely of unsaturated polyester resin, the number-average molecular weight can be determined from the endgroup analysis. The effects of f_{S_0} on the molecular weight of the soluble part of the polyester resin, \bar{M}_{SOL} , is shown in Table 3. The molecular weight of the soluble portion should decrease

with conversion of the fumarate double bond according to the present theory. \bar{M}_{SOL} decreases with the q_0 up to $f_{\text{S}_0} = 0.6 \sim 0.7$, but it increases in the region above $f_{\text{S}_0} = 0.7$. The increase in \bar{M}_{SOL} at the higher f_{S_0} does not agree with the general observations by other investigators that the conversion of fumarate double bonds increases with f_{S_0} . The effects of f_{S_0} on the molecular weight of the soluble part determined by gel-permeation chromatography are also shown in Table 3. The results show the same relationship as the results from endgroup analysis. The sharp increase in \bar{M}_{SOL} at the higher levels of f_{S_0} are more pronounced.

It is predicted from these results that the production of the styrene homopolymer may occur at higher f_{S_0} , because the amount of uncross-linked soluble polyester resin is more than that expected. Funke et al. [4] raised the question of whether free chains of polystyrene are formed in addition to the crosslinked copolymer chain because they observed that turbidity sometimes developed after curing of the polyester chain. However, they did not find evidence for the presence of the styrene homopolymer by liquid-liquid distribution chromatography of the addition polymers isolated from the hydrolysis product of the cured resin. Katz and Tobolsky [12] have predicted the formation of the styrene homopolymer in the nontransparent resin obtained after the cure.

The isolation of styrene homopolymer is an important point in the present study. A typical Bisphenol-type polyester resin was used. A 0.2550-g portion of the extracted resin from the cured resin of experiment 3 in Table 1 was analyzed by elution chromatography with a silica gel-packed column. First the column was eluted with methanol and subsequently with chloroform. The resin from the methanol-soluble fraction was 0.1917 g (75.18 wt %) and the resin from the chloroform-soluble fraction was 0.0425 g (16.67 wt %). The residual 8.15 wt % of the resin was absorbed strongly on the silica gel and not extracted by further elution with chloroform. The chemical structure was analyzed by infrared spectroscopy for each fraction. The results are shown in Fig. 3, and the spectra of the standard unsaturated polyester resin [Resin B(2)-4] and polystyrene are shown in Fig. 4. The infrared spectrum for the methanol-soluble fraction is the same as that of the standard polyester resin with the exception of a few bands, including a band at 690 cm^{-1} due to the styrene unit. The infrared spectrum for the chloroform-soluble fraction is the same as that for polystyrene with the exception of the very weak absorption at 1260 cm^{-1} which appears as a strong absorption in the infrared spectrum of the

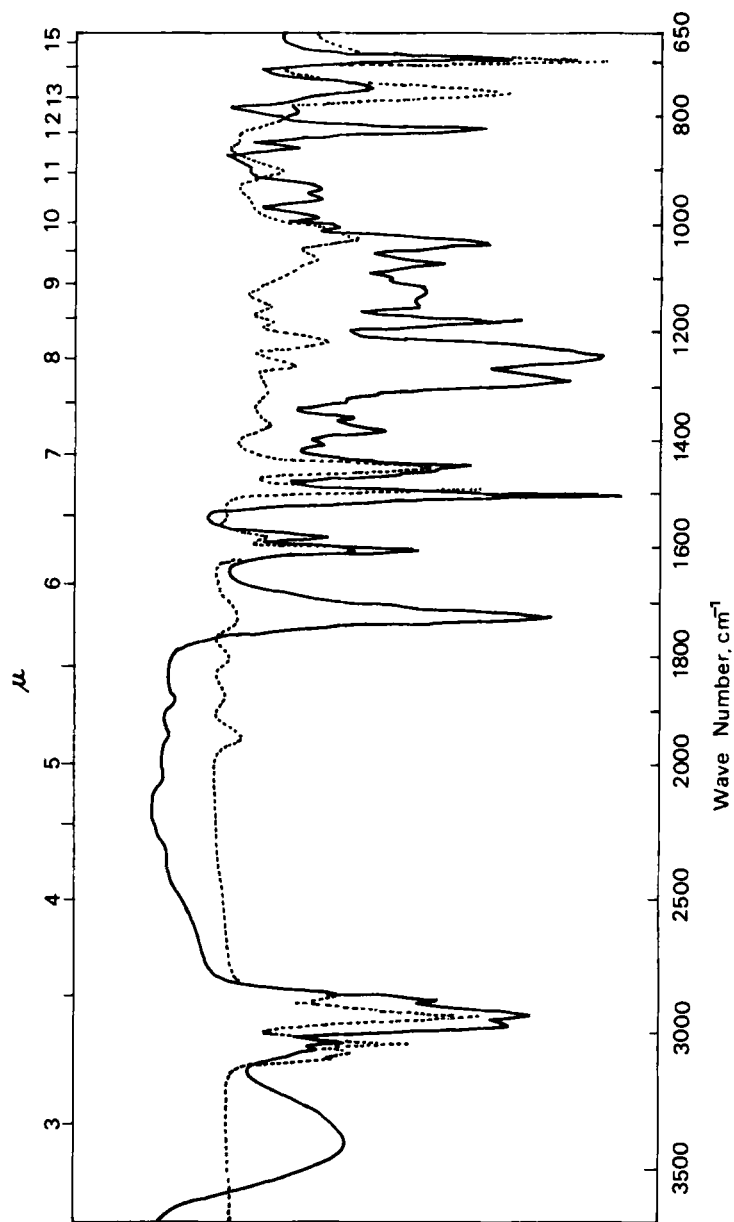


FIG. 3. Infrared spectra for (—) the methanol-soluble fraction and (---) the chloroform-soluble fraction.

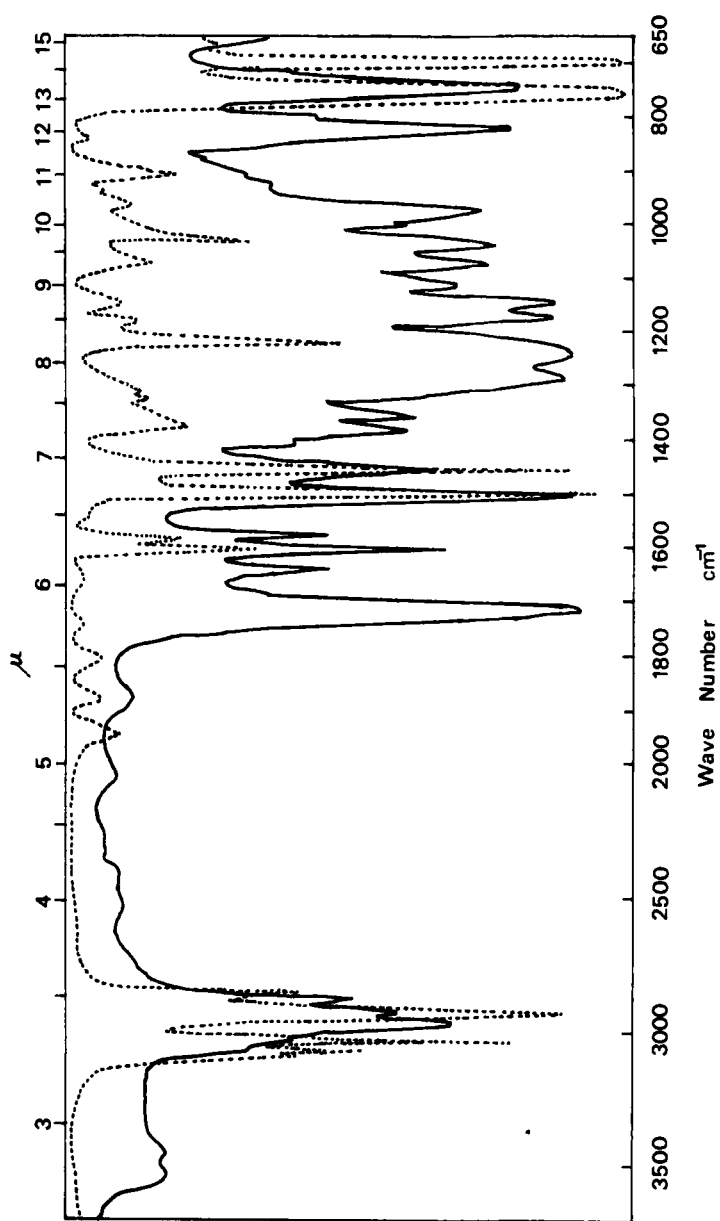


FIG. 4. Infrared spectra for (—) the standard unsaturated polyester resin [Resin No. B(2)-4] and (---) standard polystyrene.

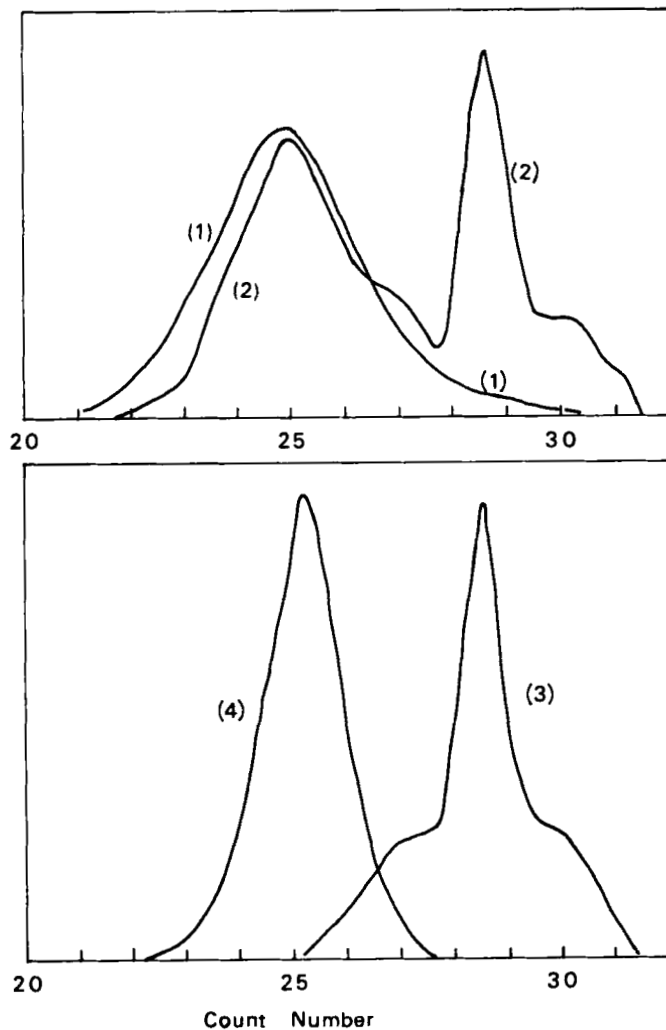


FIG. 5. Distribution curves by the gel permeation chromatography: (1) polyester resin B(2)-4; (2) extracted resin; (3) methanol-soluble fraction; (4) chloroform-soluble fraction.

standard polyester resin. Elemental analysis for C and H of the chloroform-soluble fraction showed: C, 91.8%; H, 7.8% (calcd for C_8H_8 : C, 92.26%; H, 7.7%). Each fraction was analyzed by gel-permeation chromatography (Fig. 5). Distribution curves were compared with

TABLE 4. Number-Average Molecular Weight

	\overline{M}_n	
	By gel permeation chromatography	By endgroup analysis
Starting polyester resin B(2)-4	2351	2794
Extracted resin	1284	885
Methanol-soluble fraction	430	—
Chloroform-soluble fraction	1756	—

that of the starting polyester resin, B(2)-4. The number-average molecular weight determined by gel-permeation chromatography and endgroup analysis are shown in Table 4. The molecular weight of the chloroform-soluble fraction is much higher than that for the methanol fraction. These results provide support for the supposition that styrene homopolymer is produced as a by-product in copolymerization of styrene with unsaturated polyester resins. The methanol-soluble fraction contains some styrene units, although it is still unknown whether it is due to styrene homopolymer or polystyrene units linked to the polyester chain.

On assuming that all the polystyrene component in the extracted polyester resin is present as homopolymer, the content of the polyester resin was determined by infrared spectroscopy. The calibration curves were obtained by plotting the percent of the area of the band at 1720 cm^{-1} of the total areas of the bands at 1720 cm^{-1} and 690 cm^{-1} against the weight percent of the polyester resin in the resin mixture of polyester resin and polystyrene. The band at 1720 cm^{-1} is used as a specific band for polyester resin and the band at 690 cm^{-1} is used as a specific band for polystyrene. Several typical calibration curves are shown in Fig. 6.

Another method to determine the purity of polyester resin in extracted resin is the analysis of saponification number. The purity of polyester resin determined by the infrared spectroscopy and the saponification number decrease with f_{S_0} , as shown in Table 3. The infrared spectroscopy and the saponification number method give nearly the same results. At f_{S_0} higher than 0.6-0.7, the purity of polyester resin decreases. The change is quite pronounced for resins

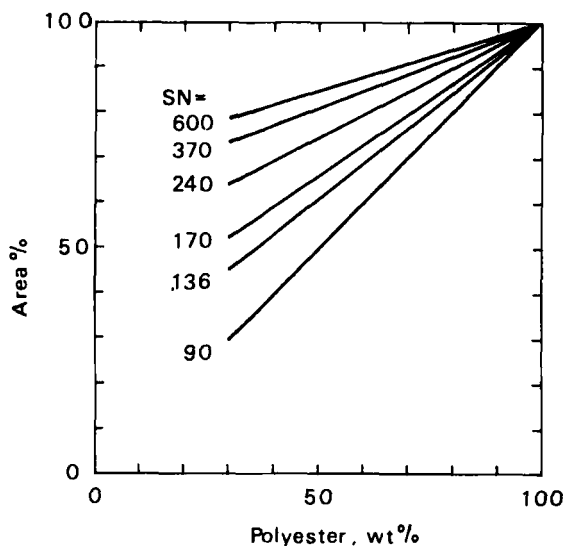


FIG. 6. Calibration curves by the infrared spectroscopy for the weight % of unsaturated polyester resin in the resin mixture of unsaturated polyester resin and polystyrene.

having low \bar{M}_0 , such as resins B(2)-5 and G-3, but it is moderate for resin having large \bar{M}_0 , such as resins B(15) and G-9. The amount of the extracted polyester resin was corrected for by the infrared spectroscopy or the saponification number method, and the conversion of fumarate double bond was recalculated by using the corrected values of the extracted polyester resin. W_{IR} and W_{SN} are the corrected soluble portion of polyester resin and q_{IR} and q_{SN} are the corrected conversion of fumarate double bond, where the subscripts denote the method of correction.

The effects of f_{S_0} on W_{IR} or W_{SN} and q_{IR} or q_{SN} are shown in Table 3, and the relationships between f_{S_0} and q_{IR} or q_{SN} are shown in Figs. 7-10. With increasing f_{S_0} , W_{IR} or W_{SN} decrease and q_{IR} or q_{SN} increase, and both the W and q level off at the higher regions of f_{S_0} . The values of q_{IR} or q_{SN} for the unsaturated polyester resins

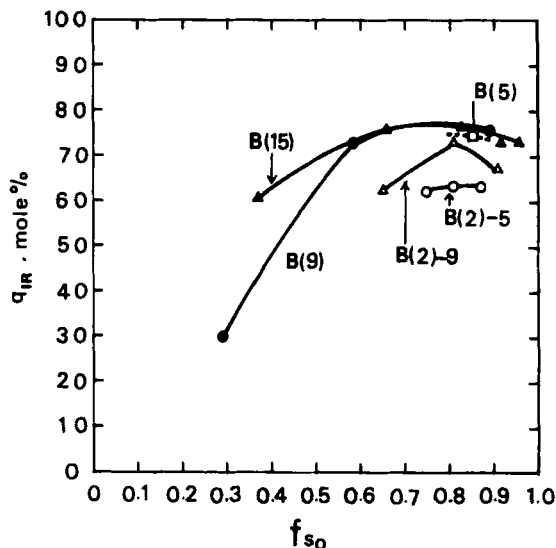


FIG. 7. Relationship between f_{S_0} and q_{IR} for Bisphenol-type resins.

having high \bar{M}_0 levels off at the lower levels of f_{S_0} , but the values for the resins having low \bar{M}_0 increase at higher levels of f_{S_0} . From these results the effect of the chemical structure of unsaturated polyester resin on the conversion of fumarate double bond can be compared by q_{IR} or q_{SN} at the region where the values of q_{IR} or q_{SN} are in plateau. The corrected values, q_{IR} or q_{SN} , are compared at 50 ± 0.5 wt % of the initial concentration of styrene for all polyester resins as shown together with q_0 in Table 2.

In the Bisphenol-type resins all the polyester resins modified by neopentylglycol, propylene glycol, hydrogenated Bisphenol A, β -hydroxyethyl terephthalate, succinic acid, and adipic acid gave the same levels of corrected values of the conversion of fumarate double bond, i.e., q_{IR} or $q_{SN} = 60 \sim 70$ mole %. However, if the resin is modified by a polyoxypropylene unit adducted to Bisphenol A, the conversion of fumarate double bond increases up to q_{IR} or $q_{SN} = 73 \sim 76$ mole %. For the standard Bisphenol-type resin, the effect

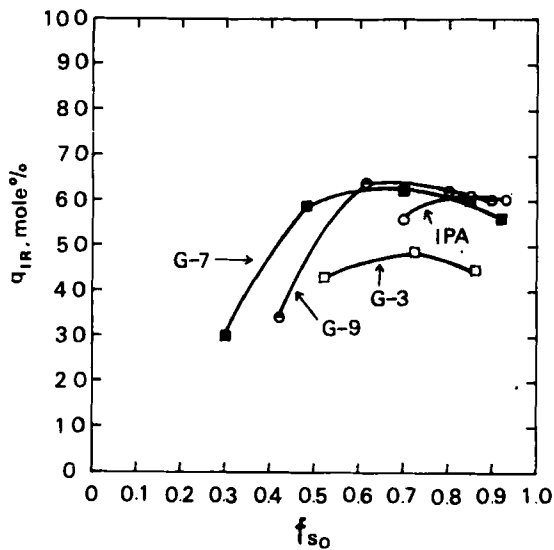


FIG. 8. Relationship between f_{S_0} and q_{IR} for Iso-type and G-type resins.

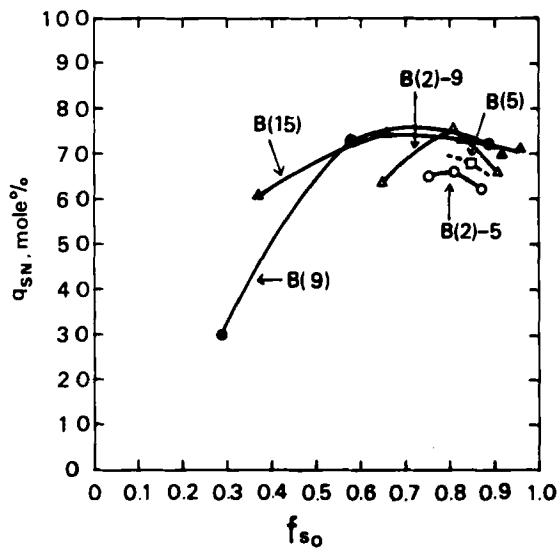


FIG. 9. Relationship between f_{S_0} and q_{SN} for Bisphenol-type resins.

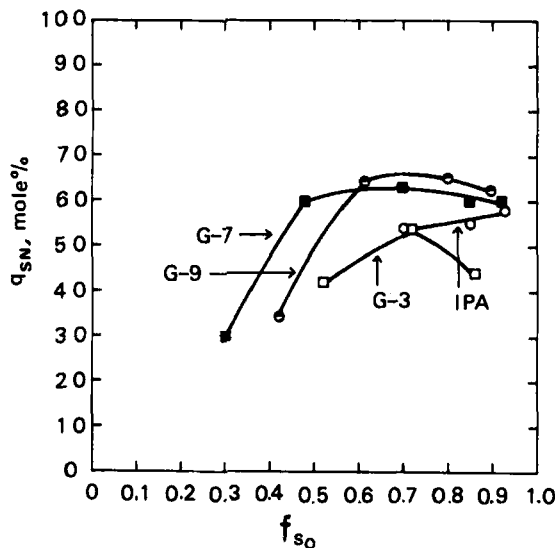


FIG. 10. Relationship between f_{S_0} and q_{SN} for Iso-type and G-type resins.

of the number-average degree of polyesterification \bar{x} on the conversion of fumarate double bond is shown in Fig. 11. At $\bar{x} < 5$, q_0 increases slightly with \bar{x} but q_{IR} and q_{SN} are located at the same level. At $\bar{x} > 5$, q_0 , q_{IR} , and q_{SN} all decrease with \bar{x} .

In the polyester resin of propylene glycol fumarate, the fumaric acid is modified with adipic acid, isophthalic acid, and phthalic acid anhydride. The corrected conversion of fumarate double bond for these modified resins follows the order of adipic > isophthalic > phthalic > unmodified, ranging from 60 to 45 mole %. The polyester resin prepared from chlorendic acid anhydride (Resin HETA) gives the lowest conversion of fumarate double bonds.

The crosslinking of unsaturated polyester resins with styrene proceeds by a radical process to form a three-dimensional network. In the early stages of the copolymerization the polymer is an alternating copolymer. Before the formation of a highly crosslinked network, the resin is soft, and there are some spaces for styrene monomer to react with unreacted fumarate double bond in the network. After the network becomes rigid and compact, diffusion of the styrene

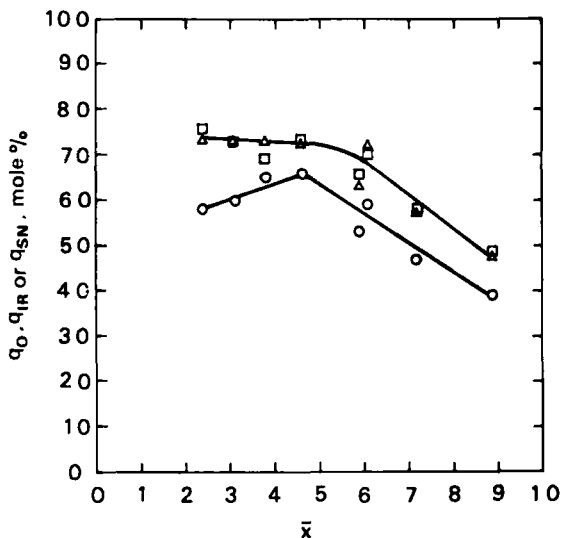


FIG. 11. Relationship between \bar{x} and (\circ) q_0 , (Δ) q_{IR} , or (\square) q_{SN} for Bisphenol-type resins.

monomer to the fumarate double bonds in the rigid network is very difficult, but the styrene monomer can react with either polystyrene radicals linked to the polyester chain or free polystyrene radicals newly generated outside the network. The latter reaction gives the styrene homopolymer which may be formed preferentially at the higher levels of f_{S_0} , especially at the later stages of copolymerization. The formation of the styrene homopolymer is unfavorable in polyester resin having large M_0 . The network formed is so loose and spacious that contact of the styrene monomer with the fumarate double bonds or the polystyrene radical linked to the polyester resin is easy. The bulky group such as chlorine group in the Het acid-type resin hinders the styrene radical to attack the fumarate double bonds. The phthalate resins and the propylene glycol fumarate polyester resin produce a compact crosslinked network at low conversion of fumarate double bond.

According to Flory [10], the effective number of chains in a real network is given by

$$\nu_e = \nu(1 - 2\bar{M}_0/\bar{M}_n) \quad (2)$$

or

$$\nu_e = \nu (1 - 2/\bar{x}) \quad (3)$$

where ν is the number of crosslinked units, \bar{M}_0 is the molecular weight per crosslinked unit, and \bar{M}_n is the molecular weight of the starting polyester resin. At a fixed molecular weight for \bar{M}_0 , ν_e will increase with \bar{M}_n . The unsaturated polyester resin providing a higher effective crosslinking density forms a complete network before all the fumarate double bond is reacted with styrene. The higher the crosslinking density, the more compact the network of the crosslinked polymer. As a result, the conversion of fumarate double bond is lowered. At a fixed molecular weight \bar{M}_n , ν_e will decrease with \bar{M}_0 . The polyester having a large \bar{M}_0 produces low-density networks even if \bar{M}_n is relatively large.

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