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Re-examination of the Crosslinking Process in Styrene-Unsaturated Polyester Systems

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ABSTRACT

The network structure of a range of styrene-unsaturated polyester networks was investigated by degradative and spectroscopic studies, sol-gel analysis, and dynamic mechanical measurements. The results show that in addition to styrene-fumarate copolymerization, a fumarate-fumarate crosslinking reaction occurs when the styrene concentration is low. The extent of this reaction was found to be dependent on the proximity of the fumarate units to one another, and on the curing conditions employed. Although the sol-gel studies were qualitatively consistent with these observations, a quantitative analysis was not successful due to deviations of the polyester networks from the model.

INTRODUCTION

A clear understanding of the nature of the copolymerization process in the crosslinking of styrene-unsaturated polyester systems has been attained [1-5] only in the last decade. Most of this information was obtained [1-4] by chemical studies involving the alkaline degradation

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of the polyester networks. The analysis of the styrene-fumaric acid copolymer chains, isolated by this technique, led to the conclusion that the styrene and fumarate units tend to copolymerize rather than homopolymerize [1-4]. In particular, these studies suggested that homopolymerization of the fumarate unsaturation is unlikely, even when the styrene concentration is low [1, 3]. This generally accepted viewpoint is at variance with literature evidence [5-11] for a cross-linking reaction between the fumarate units themselves. From the latter studies, it would appear that this fumarate-fumarate crosslinking reaction is more correctly viewed as the dimerization [6, 11] of fumarate unsaturation, rather than true homopolymerization. Furthermore, it may be deduced that this fumarate-fumarate reaction mainly occurs after the copolymerization stage [10].

The present work provides further evidence for a fumarate-fumarate crosslinking reaction during polyester network formation, through chemical, sol-gel and dynamic mechanical studies.

EXPERIMENTAL

The polyesters were prepared from the respective dioic acids and diols (see Table 1 for the abbreviated code of these units) via standard azeotropic polycondensation techniques and are denoted by a code consisting of the abbreviations used for the dioic acid and diol units. Additional details of the polyesters used in the present work have been given previously [12]. The network samples were prepared by the copolymerization of styrene with the appropriate amount of polyester. Unless so specified in the text, the samples were gelled at 60°C for 24 hr by using 0.5 wt % benzoyl peroxide, followed by post-curing at 150°C for 1.5-2.0 hr. The networks are designated by the polyester code, followed by the percentage of styrene in the dry specimen.

Network specimens were degraded by the alkaline hydrolysis method described by Bohdanecky et al. [1]. The conversion of the styrene and fumaric acid units to isolatable copolymer, thus determined, provides a simple measure of the extent of copolymerization.

Other specimens were milled and pressed into KBr disks and the infrared (IR) spectra recorded. From a comparison of the optical densities of the fumarate unsaturation band (at 980 cm^{-1}) [13, 14] and maleate unsaturation band (at 1410 cm^{-1}) [13] in the uncross-linked and crosslinked polyesters, the degree of conversion of the fumarate and maleate unsaturation was determined, the peaks in the region 1100-1200 cm^{-1} being used as internal standards [14].

The degree of conversion of the fumarate unsaturation was also determined by a modified form of the method described by Alekseeva et al. [7]. This method involves the acid hydrolysis of milled network

TABLE 1. Compositional Details of the Polyesters

Polyester code ^a	Mole fraction of the unsaturated dioic acid	Number-average molecular weight
FA/DEG/CA	0.50	770
FA/DEG/Ox	0.50	697
FA/DEG/Mal	0.50	693
FA/DEG/SA (1)	0.50	1528
" (5)	0.50	952
" (6)	0.50	718
" (7)	0.50	1540
" (8)	0.50	3192
" (9)	0.50	705
" (11)	0.25	2137
" (12)	0.35	1727
" (13)	0.60	1807
" (14)	0.70	1689
" (15)	0.10	1664
" (16)	0.50	1811
" (17)	0.50	792
MA/DEG (1) ^b	1.00	1640
FA/DEG/PA	0.50	1596
FA/DEG/IPA	0.50	1497
FA/DEG/TPA	0.50	1750
FA/TEG/PA	0.50	858
FA/PD/PA	0.50	1288
FA/PMD/PA	0.50	1595
FA/HMD/PA	0.50	1670

^aThe codes for the diol and dioic acid units are: fumaric acid (FA), maleic acid (MA), carbonic acid (CA), oxalic acid (Ox), malonic acid (Mal), succinic acid (SA), orthophthalic acid (PA), isophthalic acid (IPA), terephthalic acid (TPA), 1,3-propane diol (PD), 1,5-pentane diol (PMD), 1,6-hexane diol (HMD), diethylene glycol (DEG) and triethylene glycol (TEG).

^bThe degree of isomerism of the maleate unit to fumarate was found by NMR techniques to be 48%.

samples with concentrated sulfuric acid. The unpolymerized fumaric acid, thus freed from the network, is then quantitatively determined by the method of Ioffe [15]. Due to the fact that the diol is also oxidized by permanganate, the method of Alekseeva et al. [7] was modified by introducing additional redox stages following the acid hydrolysis of the network. These steps involved the selective oxidation of the diol with excess dichromate (at 60°C for 20-30 min), the quantitative reduction of the dichromate ions remaining by addition of excess sodium sulfite [16], followed by the removal of the excess SO₂ (by passing a vigorous stream of nitrogen through the solution for one hr [16]). The fumaric acid was then quantitatively determined by the permanganate oxidation method of Ioffe [15] as discussed by Alekseeva et al. [7].

Sol-gel studies of the networks were performed by extracting milled samples with chloroform in a Soxhlet extraction apparatus (for 24 hr) and determining the weight of soluble material.

The dynamic mechanical properties of network specimens (prepared in the form of rods) were obtained on a freely oscillating torsion pendulum [17], operated near 1 Hz. Three measures of the glass transition temperature T_g ($\tan \delta$), $T_g(10^8)$, and $T_g(\text{MP})$, were determined from the loss tangent ($\tan \delta$), and shear modulus (G') curves, as described elsewhere [18] and were averaged to give \bar{T}_g .

The shear modulus in the rubbery region was determined at the temperature $T = T_g(10^8) + 60$, and is expressed as G'/T_d , where d is the polymer density.

RESULTS AND DISCUSSION

Figure 1 shows the variation of \bar{T}_g with the styrene concentration in networks formed from MA/DEG(1) (which contained 48% fumarate isomer (Table 1) and five FA/DEG/SA polyesters with varying fumarate/succinate ratios. (The number-average molecular weight of the polyesters was nearly constant.) According to the results of alkaline hydrolysis studies [1-4], the conversion of the fumarate unsaturation to crosslinks is nearly quantitative when the mole fraction of styrene is greater than 0.6. This value corresponds to 18 wt % styrene in FA/DEG/SA(11)-based networks and ranges up to 37 wt % styrene for FA/DEG/SA(14). Therefore, in networks containing more than 60 mole % styrene, the crosslink density should be controlled by the fumarate concentration. Since T_g is approximately linear with the crosslink density [19] provided that the chemical composition of the network is invariant, \bar{T}_g should increase when

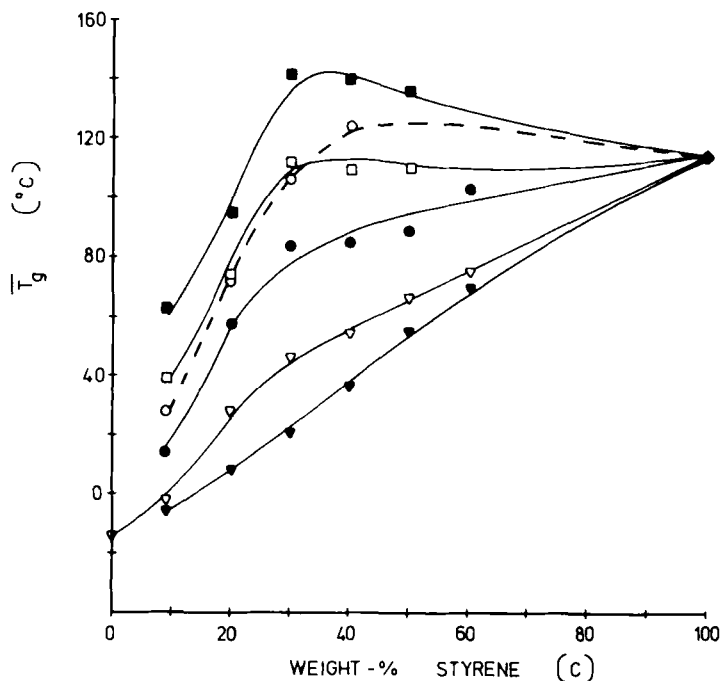


FIG. 1. \bar{T}_g vs. styrene concentration in networks formed from (▼) FA/DEG/SA(11), (▽) FA/DEG/SA(12), (●) FA/DEG/SA(16), (◻) FA/DEG/SA(13), (■) FA/DEG/SA(14), and (○) MA/DEG(1).

the fraction of fumarate in the polyester is raised, in agreement with the results in Fig. 1. The values of \bar{T}_g for the MA/DEG(1)-based networks are lower than those for the FA/DEG/SA(14) networks, even though the former polyester contains more unsaturated units. This observation is consistent with the reactivity ratios [20] and the results of chemical studies [1, 4], which show that the maleate unit does not copolymerize well with styrene.

The alkaline hydrolysis studies also suggest [3, 4] that when the mole fraction of styrene is less than 0.6, the crosslink density is approximately equal to the styrene concentration (since the styrene and fumarate units have a tendency towards alternating copolymerization [20]). Figure 1 shows, however, that in this region, \bar{T}_g also increases as the fraction of fumarate in the polyester is raised. It might be considered that this is due to a stiffening of the polyester

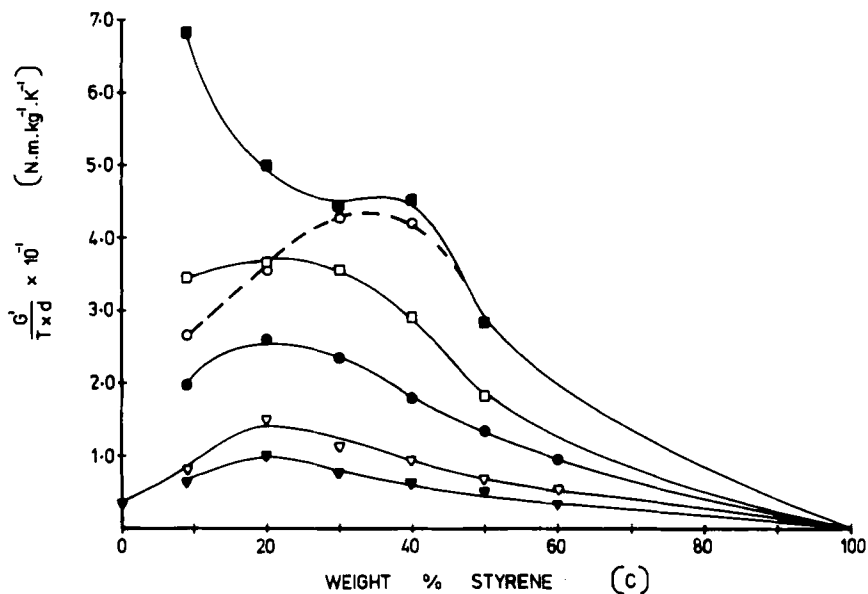


FIG. 2. G'/T_d in the rubber region of the FA/DEG/SA-based networks vs. styrene concentration. Symbols as in Fig. 1.

chains by the unreacted unsaturation, since a similar effect has been found [21] in the corresponding uncrosslinked polyesters. The data in Fig. 1 for the MA/DEG(1) networks suggest, however, that this stiffening effect cannot fully explain the observed behavior. This follows, since the \bar{T}_g values for the MA/DEG(1)-based networks are below those for the FA/DEG/SA(13)- and FA/DEG/SA(14)-based networks (up to 30 wt % styrene) despite the fact that the former polyester contains more unsaturated units. Therefore it may be suggested that \bar{T}_g increases when the fraction of fumarate in the polyester is raised, due to the additional fumarate-fumarate cross-linking.

Figure 2 shows the variation in the rubbery modulus with the styrene concentration for the networks relating to Fig. 1. According to the theory of rubber elasticity [22], G' is approximately proportional to the crosslink density. Above 30 wt % styrene, Fig. 2 shows that G'/T_d decreases when the styrene concentration is raised, and that G'/T_d increases when the fraction of fumarate units in the polyester is raised. These results are qualitatively consistent with the results from alkaline hydrolysis studies [1-4], which show that above 60

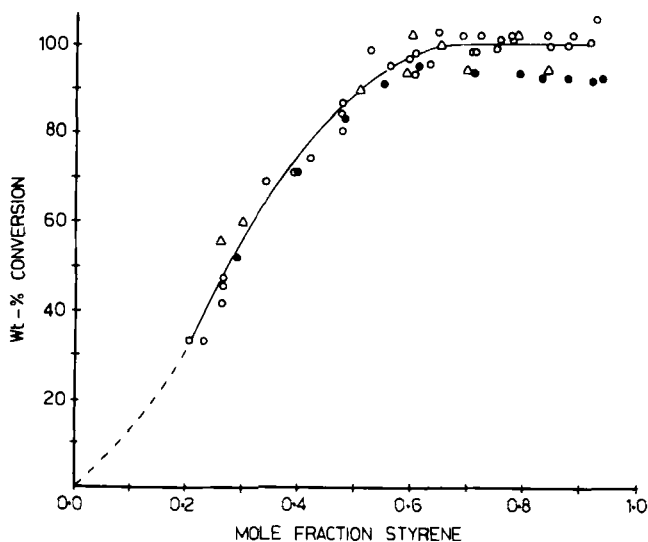


FIG. 3. Conversion of the monomer units to copolymer vs. the mole fraction of styrene in (o) the FA/DEG/SA-based networks and (Δ) in other polyester networks; (●) data of Funke et al. [3].

mole % styrene the crosslink density is controlled by the fumarate concentration. At lower styrene concentrations, however, Fig. 2 shows that G'/T_d also increases when the fraction of fumarate in the polyester is raised, despite the evidence from alkaline hydrolysis studies [3, 4] that in this region, the crosslink density should only depend on the styrene concentration. This behavior cannot be rationalized in terms of the stiffening effect of the unreacted double bonds on the polyester chains, as the rubbery moduli of the MA/DEG(1)-based networks are less than those for the FA/DEG/SA(14)-based networks. Therefore the data in Fig. 2 provide further evidence for a fumarate-fumarate crosslinking reaction.

Figure 3 shows the dependence of the conversion (to copolymer) of the styrene and fumarate units in a range of the polyester networks. The results are similar to those obtained by Funke et al. [3] for networks which were synthesized under comparable conditions to those used in the present work. Therefore Fig. 3 shows that the unusual behavior found in Figs. 1 and 2 (at low styrene concentrations) cannot be explained in terms of differences in the extent of copolymerization.

The IR spectra of FA/DEG/SA(9)/0 and some styrene copolymers of FA/DEG/SA(9) and FA/DEG/SA(6) (these polyesters were almost

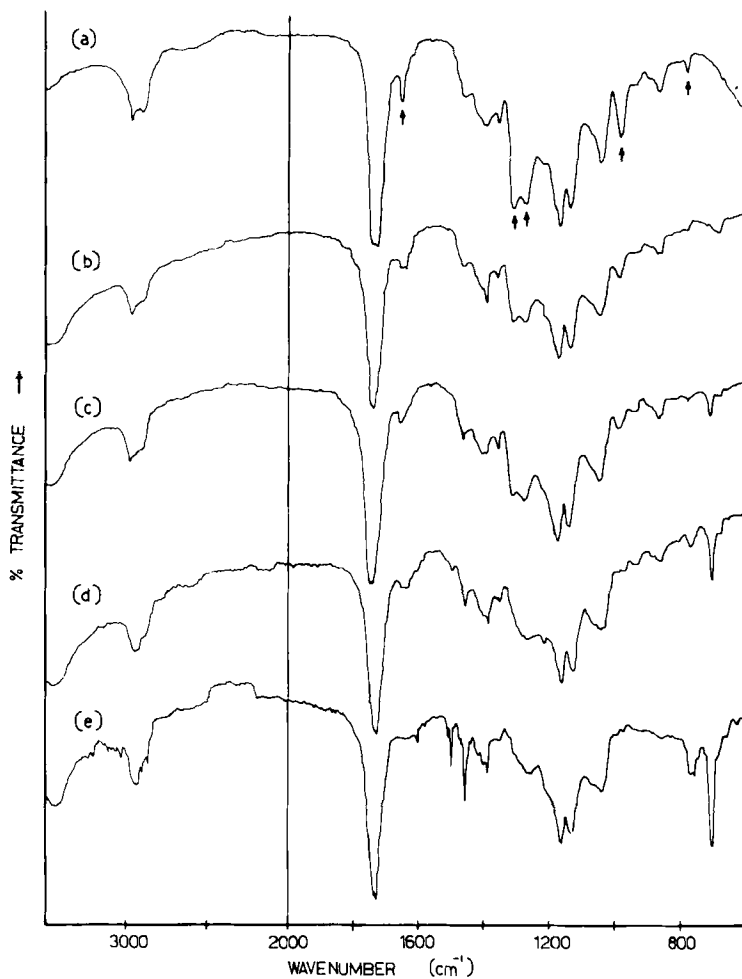


FIG. 4. IR spectra of (a) FA/DEG/SA(9) and powdered samples from the networks (b) FA/DEG/SA(9)/0, (c) FA/DEG/SA(9)/9, (d) FA/DEG/SA(6)/20, and (e) FA/DEG/SA(6)/40.

identical) are shown in Fig. 4. The spectrum of FA/DEG/SA(9) is included in this figure, for comparison. The intensity of the bands sensitive to fumarate unsaturation [10, 13, 14] at 770, 980, 1270, 1310, and 1650 cm^{-1} are considerably reduced (with respect to the internal standards in the region 1100-1200 cm^{-1} [14] in

TABLE 2. Conversion of the Fumarate (and Maleate) Units to Crosslinks Determined from the IR Spectra

Polyester code	Conversion (mole %) at various styrene levels ^a						
	0	9.1 wt %	20 wt %	30 wt %	40 wt %	50 wt %	80 wt %
FA/DEG/SA(6)			87 (74)		89 (95)		
" (7)						94 (96)	
" (8)		86 (35)					
" (9)	46 (0)	60 (35)					
" (13)		84 (28)	86 (63)	92 (86)			
" (14)		74 (24)	77 (57)	80 (81)	90 (92)	94 (95)	
MA/DEG(1)		49 N.A. ^b		58 N.A. ^b			
FA/DEG/IPA	78 (0)	78 (39)					
FA/TEG/PA						92 (94)	
FA/PD/PA		59 (34)				90 (96)	84 ^c (97)

^aThe values in parentheses were calculated from the alkaline hydrolysis results of Funke et al. [3].

^bNot available.

^cThis result may be an underestimate, due to overlap of the 980 cm^{-1} fumarate band with neighboring bands of the styrene units.

FA/DEG/SA(9)/0 and FA/DEG/SA(9)/9 compared with the linear polyester; while in FA/DEG/SA(6)/20, only the bands at 1270 and 1650 cm^{-1} can be readily observed. In the FA/DEG/SA(9)/40 network, there is little evidence of the fumarate unsaturation bands.

Table 2 lists the degree of conversion of the fumarate unsaturation,

TABLE 3. Conversion of the Fumarate Units to Crosslinks Determined by the Acid Hydrolysis Method^a

Polyester code	Conversion (mole %) at various styrene levels			
	0	9.1 wt %	20 wt %	30 wt %
FA/DEG/CA		85 (31)		
FA/DEG/Ox		80 (32)		
FA/DEG/Mal		67 (34)		
FA/DEG/SA(1)	61 (0)	76 (35)		
" (5)		63 (35)		
" (6)		58 (35)	84 (74)	92 (91)
" (7)		70 (35)	87 (74)	
" (8)		82 (35)	88 (74)	
" (9)	49 (0)	63 (35)		
" (11)		69 (63)		
" (12)	51 (0)	75 (49)		
" (13)		78 (28)	88 (63)	
" (14)		73 (24)	85 (57)	85 (81)
" (16)		73 (35)		
" (17)		67 (35)		
FA/DEG/PA	80 (0)	80 (39)		
FA/DEG/IPA	67 (0)	75 (39)		
FA/DEG/TPA		79 (39)		
FA/TEG/PA	71 (0)	77 (46)		
FA/PD/PA		49 (34)		
FA/PMD/PA	47 (0)	58 (38)		
FA/HMD/PA		55 (41)		

^aThe values in parentheses were calculated from the alkaline hydrolysis results of Funke et al. [3].

determined by the IR method and includes the percentage of fumarate unsaturation copolymerized with styrene, calculated from the alkaline hydrolysis results of Funke et al. [3]. For high styrene levels, both sets of data suggest that the fumarate unsaturation is almost completely reacted. However, there is a consistent discrepancy between the two methods when the styrene concentration in the network is low. Thus the spectroscopic results indicate that the degree of conversion of the fumarate unsaturation is higher than that expected if the styrene-fumarate copolymerization was the only form of crosslinking. A similar result is shown in Table 3.

It would appear that the alkaline hydrolysis method underestimates the degree of conversion of the fumarate unsaturation in networks containing low styrene mole fractions, for the following reasons. Poly(fumaric acid) is soluble in aqueous solution [8], so that poly-addition chains which contain a high percentage of polymerized fumarate units would not be isolated as a precipitate in the alkaline hydrolysis method. Since in this method, the degree of conversion of the fumarate units is calculated from the composition of the isolated copolymer, fumarate-fumarate crosslinking reactions would not be detected.

It is of interest to note that the degree of conversion of the fumarate units, determined by the acid hydrolysis studies (Table 3), increases when the molecular weight of the FA/DEG/SA-type polyesters is raised. This result may indicate that the fumarate groups at the end of the polyester chains do not homopolymerize well. Tables 2 and 3 also show that the degree of conversion increases when the fraction of fumarate units in the FA/DEG/SA-type polyesters is raised, while the fraction of copolymerized fumarate units (calculated from the alkaline hydrolysis results of Funke et al. [3]) decreases concurrently. This behavior may be explained in terms of the proximity of one unreacted fumarate unit to another. Since gel formation occurs at a low crosslink density [23], the mobility of the fumarate units should be restricted throughout most of the polymerization. Therefore fumarate-fumarate crosslinking may only occur when the fumarate units are in close proximity. Thus the probability of fumarate-fumarate crosslinking should increase when the fraction of fumarate units in the polyester is raised, which is in agreement with the results.

The occurrence of fumarate-fumarate crosslinking should also be detectable by sol-gel studies, since this reaction can link polyester chains to the gel structure. Figure 5 shows the dependence of the sol fraction, $W_1(0)$ (expressed as a weight fraction of the polyester in the network), on the styrene content in networks prepared from polyesters of varying molecular weights. $W_1(0)$ is seen to decrease when the polyester molecular weight is raised, since the probability that a particular chain contains a reacted fumarate unit (and is likely

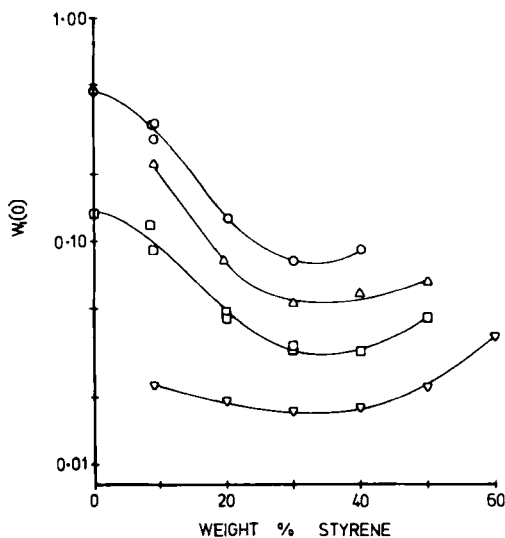


FIG. 5. $W_1(0)$ vs. styrene concentration in networks formed from (o) FA/DEG/SA(6) (and FA/DEG/SA(9)), (Δ) FA/DEG/SA(5), (\square) FA/DEG/SA(7) and FA/DEG/SA(1), and (∇) FA/DEG/SA(8).

to be connected to the gel) increases as the number of fumarate units per chain, and hence the polyester molecular weight, is raised. Figure 5 also shows that even when the polyesters were cured in the absence of styrene, the samples are predominantly composed of gel material. This provides further evidence of fumarate-fumarate crosslinking. When the styrene concentration is raised, the sol fraction decreases due to increased crosslinking of the polyester chains by styrene units. Above 30 wt % (or 60 mole %) styrene, however, the fraction of sol reaches a minimum and then increases. Since the extent of conversion of the fumarate unsaturation is almost quantitative when the resin contains more than 60 mole % styrene [1-4] (see also Table 2), the increase in $W_1(0)$ at higher levels of styrene is probably due to the presence of polystyrene molecules and crosslinked polyester chains in the sol, as was suggested by Sakaguchi and Takemoto [24].

Figure 6 shows $W_1(0)$ versus the styrene concentration in networks synthesized from polyesters having similar molecular weights but varying fumarate/succinate ratios. At low styrene concentrations, $W_1(0)$ decreases by a factor of ten when the fraction of fumarate in the polyester is raised. This result is not in agreement with the alkaline hydrolysis studies [3, 4], since they suggest that the number

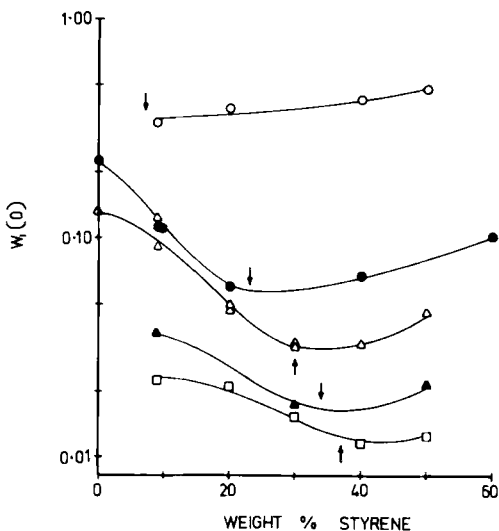


FIG. 6. $W_1(0)$ vs. styrene concentration in networks formed from (○) FA/DEG/SA(15), (●) FA/DEG/SA(12), (△) FA/DEG/SA(7) and FA/DEG/SA(1), (▲) FA/DEG/SA(13), and (□) FA/DEG/SA(14). The arrows in this figure represent the weight percentage of styrene corresponding to a styrene mole fraction of 0.6.

of crosslinks (which are randomly distributed) and hence the fraction of gel, should be approximately constant when the styrene concentration is low and invariant. Therefore the sol-gel data are consistent with a fumarate-fumarate crosslinking reaction when the styrene concentration is low (below 60 mole %).

With the exception of the FA/DEG/SA(15)-based networks, the $W_1(0)$ curves in Fig. 6 pass through a minimum, as was found in Fig. 5. The sol fraction at this point increases as the molar ratio of fumarate to succinate decreases, since the fraction of polyester chains which contain at least one fumarate unit also decreases. The minimum value of $W_1(0)$ for each polyester system occurs close to the styrene mole fraction of 0.6 (indicated by arrows in the figure), which corresponds to the region where most of the fumarate unsaturation is reacted [1-4] (see also Tables 2 and 3). At higher styrene concentrations, $W_1(0)$ increases, probably due to the presence of polystyrene molecules and crosslinked polystyrene-polyester copolymer molecules in the sol [24].

Shito [25] has theoretically derived the equation (1) relating the fraction of sol (the uncrosslinked polyester molecules) to the degree of conversion of the fumarate unsaturation:

TABLE 4. Conversion of the Fumarate Units (q) Calculated from the Sol-Gel Studies and Equation (1)^a

Polyester code	Conversion (mole %) at various styrene levels			
	0	9.1 wt %	20 wt %	30 wt %
MA/DEG(1)		27 (-)		47 (-)
FA/DEG/PA	55 (0)	55 (39)	64 (78)	70 (93)
FA/DEG/IPA	43 (0)	54, 56 (39)	71 (78)	79 (93)
FA/DEG/TPA		73 (39)	82 (78)	86 (93)
FA/TEG/PA	56 (0)	62 (46)		74 (94)
FA/PD/PA		45 (34)	59 (73)	72 (91)
FA/PMD/PA	28 (0)	43 (38)		67 (92)
FA/HMD/PA		42 (41)	64 (81)	70 (93)
FA/DEG/SA(1)	41 (0)	43 (35)		
" (5)		42 (35)	82 (74)	(102) ^b (91)
" (6)		37, 37 (35)	82 (74)	(103) ^b (91)
" (7)		52 (35)	72, 75 (74)	87, 89 (91)
" (8)		58 (35)	62 (74)	66 (91)
" (9)	26 (0)	46 (35)		

(continued)

TABLE 4. (continued)

Polyester code	Conversion (mole %) at various styrene levels			
	0	9.1 wt %	20 wt %	30 wt %
FA/DEG/SA(11)		68, 70 (63)	89 (94)	
" (12)	33 (0)	57, 58 (49)	85 (86)	
" (13)		62 (28)		86 (86)
" (14)		69 (24)	71 (57)	80 (81)
" (15)		81 (93)		
" (17)		54 (35)	94 (74)	(105) ^b (91)

^aThe values in parentheses were calculated from the alkaline hydrolysis results of Funke et al. [3]. Only the results from systems containing less than 70 mole % styrene are listed.

^bThese values were obtained from the extrapolated $q-W_1(0)$ curve.

$$W_1(0) = \frac{(1-p)^2 \{ (1-s)(1+p)^2(1-q)M_{A_1} + s(1+p)^2M_{A_2} + [1+(1-q+qs)p]^2M_B \}}{[(1-s)M_{A_1} + sM_{A_2} + M_B][1-(1-q+qs)p^2]^2} \quad (1)$$

where M_{A_1} , M_{A_2} , and M_B are the molecular weights of the unsaturated dioic acid, saturated dioic acid and diol units, respectively; p is the extent of polycondensation; s is the fraction of saturated dioic acid units in the polyester; and q is the fraction of reacted fumarate unsaturation. An alternative theory relating the sol fraction to the extent of crosslinking has been derived by Sakaguchi [26]; however, this theory is not self-consistent in its use of Flory's [22] "most probable distribution."

Table 4 lists the degree of conversion of the fumarate unsaturation (q), calculated from the experimental values of $W_1(0)$ and Eq. (1), and

TABLE 5. Influence of the Curing Conditions on the Rubbery Modulus (G'), \bar{T}_g , the Sol Fraction, and the Extent of Conversion of the Fumarate Unsaturation

Polymer code	Benzoyl peroxide (wt %)	Curing schedule ^a	$G' \times 10^{-7}$ at $T_g (10^6) + 60^\circ\text{C}$ (N/m^2)	\bar{T}_g ($^\circ\text{C}$)	Soluble material (wt %)	Conversion of fumarate (mole %)
FA/DEG/Ox/9	0.5	A	0.6 ₅	9	-	80
"	0.5	B	0.9 ₅	25	-	-
FA/DEG/PA/9	0.5	C	0.9 ₀	43	8.6 ₀	80
"	1.0	C	1.1 ₅	49	6.3 ₀	89
FA/DEG/IPA/9	0.5	C	0.6 ₀	49	9.4 ₉	75
"	0.5	D	0.8 ₅	60	7.9 ₂	85
FA/DEG/IPA/40	0.0	E	0.5 ₅	94	3.6 ₃	-
"	0.5	C	0.4 ₈	95	3.8 ₄	-
"	1.0	C	0.5 ₀	98	4.1 ₀	-
FA/PD/PA/9	0.5	C	0.8 ₆	46	12.8	59 ^b
"	0.5	D	1.5	59	9.5 ₆	75 ^b
FA/HMD/PA/9	0.0	F	0.2 ₁ ^c	-3	23.1	44
"	0.5	C	0.6 ₅	12	13.2	55
"	0.5	D	0.8 ₅	14	-	-
"	1.0	D	1.00	17	7.6 ₆	61

^aThe curing schedules were: A, 60°C (24 hr), 130°C (2 hr); B, 60°C (330 hr), 130°C (2 hr); C, 60°C (24 hr), 150°C (1.5 hr); D, 60°C (24 hr), 120°C (120 hr), 150°C (1.5 hr); E, 60°C (24 hr), 120°C (36 hr), 150°C (1.5 hr); and F, 60°C (48 hr), 120°C (120 hr), 150°C (1.5 hr).

^bThese values were calculated by the IR spectroscopic method. All other values were determined by the acid hydrolysis method.

^cMeasured at $T_g(10^8) + 100^\circ\text{C}$, due to the broad nature of the transition region.

includes the values calculated from the alkaline hydrolysis results of Funke et al. [3]. In the region of low styrene mole fractions, the sol-gel results consistently predict higher fumarate conversions than those found by Funke et al. [3], thus confirming the presence of fumarate-fumarate crosslinking. The values of q , however, are generally lower than the degree of conversion, determined by the IR and acid hydrolysis methods (compare Tables 2, 3, and 4). In part, this discrepancy may be due to the presence of crosslinked polyester molecules in the sol. Such an explanation is quite reasonable if it is accepted that dimerization is the main form of fumarate-fumarate crosslinking. At higher mole fractions of styrene, the degree of conversion of the fumarate unsaturation was underestimated by the sol-gel analysis, and is probably due to deviations of the networks from the idealized model of Shito [25], as discussed earlier.

It has been reported that an increase in the peroxide concentration [6] or prolonged postcuring [10] results in an increase in the extent of fumarate-fumarate crosslinking in polyester networks. Such an effect should therefore be detected in the viscoelastic properties by an increase in T_g and the rubbery modulus, and in sol-gel studies by a decrease in the fraction of sol material. Table 5 shows that this is generally found. The FA/DEG/IPA/40 networks are an exception to this generalization, since G' shows no systematic variation with the curing conditions, while \bar{T}_g and the fraction of sol increase only slightly when the peroxide level is raised. From these results it may be concluded that the degree of crosslinking in FA/DEG/IPA/40 is not significantly affected by increasing the peroxide concentration, as the styrene concentration (73 mole %) is sufficient for complete copolymerization of the fumarate unsaturation.

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