Structure–Property Relationships for Styrene Crosslinked Polyesters. I. Network Structure and Rubbery Elastic Modulus

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SYNOPSIS

Ten unsaturated polyester prepolymers differing by the nature of the diol, by the maleate/phthalate molar ratio, or by the chain length, were crosslinked by about 40% by weight of styrene and then analyzed by IR spectrophotometry, solid state NMR, and rubbery elasticity measurements.

The spectrometric measurements revealed a practically complete conversion of the styrene/fumarate copolymerization. The rubbery elastic modulus varies in a complex way with the presumed network structure.

A non-ideality factor f was defined from the current theories; f is a decreasing function of the average number of flexible bonds between crosslinks.

The networks based on dimeric diols display a practically ideal behavior.

The influence of dangling chains, corresponding essentially to polyester chain ends, is taken into account by the Graessley's formula in which trifunctional and tetrafunctional crosslinks are distinguished. A method for the estimation of the nature and weight fraction of dangling chains was proposed.

INTRODUCTION

Very important physical properties of crosslinked polyesters such as the free volume fraction and the glass transition temperature T_g are presumably under the direct control of the network structure.[1-4] This latter is usually represented by the average molar weight of the network segment between consecutive crosslinks M_c, or by the crosslink density n.

The industrial styrene crosslinked polyesters differ noticeably from ideal networks. Thus, other parameters such as the size and concentration of dangling chains, intramolecular cycles, and other structural irregularities are to be taken into account.

It is not very easy to determine the network structure from the analytical data usually available; for instance DSC[5,6] and IR,[6,7] generally give information on the consumption of the reactive species (styrene and maleic double bonds), but not on the structure of the resulting copolymer. Thus, the sequence distribution of styrene and fumaric monomer units and the concentration of dangling chains resulting from the interruption of the copolymer growth are generally ignored in the studies of structure–property relationships. A method based on the complete hydrolysis of the ester groups, leading to a linear styrene-fumarate acid copolymer, was proposed by Flodin and Bergmark,[8] to establish these characteristics, however it is time-consuming and cannot be used in routine determinations.

Another way consists of making a model of the network structure based on the accessible structural parameters (prepolymer composition and chain length, styrene concentration, double bond consumption, etc.) and to compare this model to experimental data on properties directly linked to the network structure, such as rubbery elastic modulus or glass transition temperature.

This method was chosen here to study a series of samples differing essentially by the prepolymer

composition or chain length. The results of this preliminary study will be then used to characterize the effects of hydrolytic aging on polyester composite matrices.

EXPERIMENTAL

Materials

All the materials under study were supplied by NORSOLOR. The prepolymers were of the maleate/phthalate type.

Four types of diols were investigated: propylene glycol (PG), dipropylene glycol (DPG), diethylene glycol (DEG), and neopentyl glycol (NPG).

In the case of PG systems, various values of the phthalate/maleate molar ratio $p/(1-p)$ and of the prepolymer chain length were studied. In one sample (G), phthalate was replaced by tetrahydrophthalate (THP).

The weight fraction of styrene in the initial reactive mixture was 0.45 (45%), but about 5% was lost by evaporation during the cure and postcure operations. The residual styrene weight fraction s was determined by IR spectrophotometry. All the available analytical data on the sample under study will be reported in the table of results.

The initiating mixture was composed of 1.5% methylethylketone peroxide and 0.6% cobalt octoate in solution in terbutylphthalate (AKZO). The reactive mixture was degassed under primary vacuum and then cast in a metallic mold. After polymerization for 3 h at ambient temperature, the plates of 250 × 180 × 0.7 mm were demolded and then postcured between glass plates for 10 h at 80°C, followed by 2 h at 120°C. No residual exotherm was found by DSC after this curing cycle, showing that the conversion reached an asymptotic value.

Analysis

The IR spectra were taken on KBr pellets, using a BRUKER IFS 88 IRGT apparatus.

The NMR spectra of the starting reactive mixture were taken with a high resolution BRUKER 300 MHz apparatus, using the heteronuclear decoupling technique by proton irradiation. The NMR spectra of the crosslinked samples were taken with a BRUKER 250 MHz (63 MHz for ^{13}C), using a solid state probe and the cross-polarization magic angle spinning technique.

The acidic chain ends were titrated by KOH in a methanol solution. The alcoholic chain ends were

first converted into ester groups by reaction with acetic anhydride whose excess was titrated by KOH. Both titrations were made according to IUPAC recommendations.[9]

Steric exclusion chromatographic measurements were performed on tetrahydrofuran solutions, using microstyragel columns and a refractometric detection with a calibration which included various polystyrene standards and styrene.

Physical properties

The glass transition temperature T_g and the rubbery shear modulus G'_r were determined by viscoelasticimetry, using a BRABENDER torsiometer at 5 Hz, 1° angle amplitude, between $-120°C$ and $+180°C$. T_g was arbitrarily taken at the maximum of the loss factor tan δ, and G'_r was determined at $T_g + 30$ K. The density ρ at this temperature was estimated from room temperature measurements and previously published data on cubic expansion coefficients.[1]
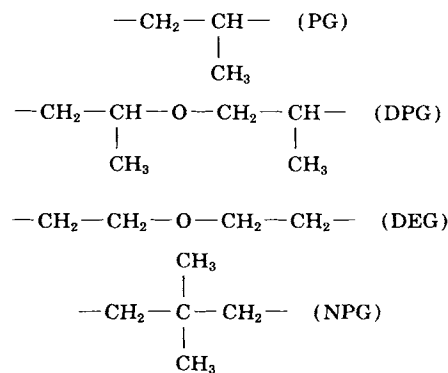
RESULTS AND DISCUSSION

Constituent Repeat Unit (CRU)

For an ideal network, the simplest structural unit (SSU), representative of the whole network structure, would be based on one diol structural unit:
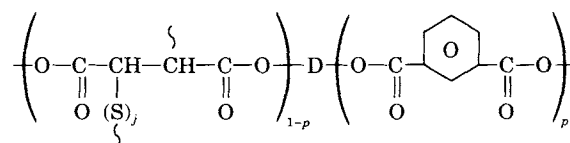
where S is the styrene monomer unit and D the diol moiety:

Each SSU is composed of m_0 grams of polyester and m_s grams of styrene. Its molar mass is

$$m = m_0/(1 - s)$$

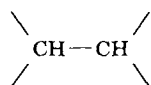s being the styrene mass fraction.

The number j of styrene monomer units per SSU is

$$j = \frac{m_0}{104} \cdot \frac{s}{(1 - s)(1 - p)} \qquad (1)$$

In the ideal network, free of chain ends, the concentration of elastically active subchains (EAS) would be

$$\nu_i = M_{ci}^{-1} = \frac{2 \cdot (1 - p)}{m} \qquad (2)$$

All the crosslinks would be of the "tetrafunctional" type, e.g., linked to four EAS:

$$\diagdown \negmedspace\negmedspace CH \negmedspace - \negmedspace CH \negmedspace \diagup$$

If b is the overall concentration of dangling chains, it could be written, for the real network:

$$\nu = M_c^{-1} = M_{ci}^{-1} - \frac{b}{2} \qquad (3)$$

The concentration b is composed of two terms

$$b = b_s + b_p \qquad (4)$$

where b_s is the concentration of chain ends created by the maleate/styrene copolymerization and b_p is the concentration of polyester chain ends.

$$b_p = I_a + I_{OH} \qquad (5)$$

where I_a and I_{OH} are the respective concentrations of acidic and alcoholic chain ends determined by chemical titration.

The value of b_s can be in principle determined by the method of Flodin and Bergmark.[8] According to the experimental data reported by these authors, the order of magnitude of b_s would be 30–100 ppm, against 200–1100 ppm for b_p.

If b_s is neglected, it becomes interesting to take a CRU based on one initial prepolymer chain, e.g.

$$CRU = -(SSU)_q- \qquad (6)$$

where q is such as:

$$\frac{2}{b_p} = M_n = qm_0 \qquad (7)$$

M_n being the number average molar weight of the prepolymer.

This CRU contains two dangling chains and $q \cdot (1 - p)$ crosslinks including $n_q = q \cdot (1 - p) - 2$ "tetrafunctional" crosslinks and $n_s = 2$ "trifunctional" crosslinks, these latter being connected to one dangling chain.

Here, the number of elastically active subchains (EAS) would be:

$$N = 2 \cdot q \cdot (1 - p) - 1 \qquad (8)$$

and

$$M_c = \frac{M}{N} = \frac{M_n}{(1 - s) \cdot N} \qquad (9)$$

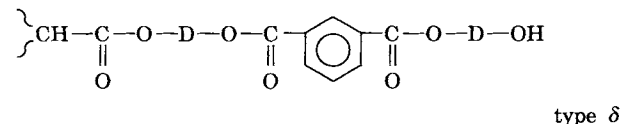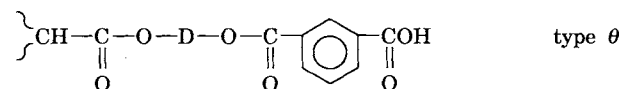where M is the molar mass of the CRU and $M = qm$.

Polyester Dangling Chains

As will be shown in a future article, the nature and concentration of polyester dangling chains play an important role in hydrolytic aging. Estimations can be made on the basis of the following hypothesis:

1. The concentration of maleate unreacted units is negligible, as it will be seen in section 4 of this article.
2. The phthalate (P)–maleate (M) copolyester is essentially of the alternating type.

This is a purely hypothetical situation, but it must be noted that, for simple statistical reasons, the presence of significant amounts of phthalate-phthalate sequences in dangling chains would be only consistent with high concentrations of such sequences in the whole network, which apparently was never reported.

According to these hypotheses, only four types of polyester chain ends can be found:

$$\diagdown\negmedspace CH \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace OH \qquad \qquad \text{type } \alpha$$

$$\diagdown\negmedspace CH \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace O \negmedspace - \negmedspace D \negmedspace - \negmedspace OH \qquad \qquad \text{type } \beta$$

$$\diagdown\negmedspace CH \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace O \negmedspace - \negmedspace D \negmedspace - \negmedspace O \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace \bigcirc \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} OH \qquad \text{type } \theta$$

$$\diagdown\negmedspace CH \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace O \negmedspace - \negmedspace D \negmedspace - \negmedspace O \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace \bigcirc \negmedspace - \negmedspace \underset{\underset{O}{\|}}{C} \negmedspace - \negmedspace O \negmedspace - \negmedspace D \negmedspace - \negmedspace OH$$

$$\text{type } \delta$$

The concentrations are linked by the following relations:

$$\alpha + \theta = I_a \tag{10a}$$

$$\beta + \delta = I_{OH} \tag{10b}$$

$$\theta/\alpha = \delta/\beta = [\text{Phthalate}]/[\text{Maleate}]$$
$$= p/(1-p) \tag{10c}$$

The system of equations allows the determination of α, β, θ, and δ.

Molecular Weight of Prepolymers, Dangling Chains

The experimental values of I_a and I_{OH} from chemical titrations, and of the number average molar weight of the prepolymer M_n and its polydispersity P determined by steric exclusion chromatography (SEC), are given in Table I. A value of M_n can also be derived from $(I_a + I_{OH})$.

Both values of M_n display a fair correlation (Fig. 1). The discrepancies can be at least partly attributed to some branching.[10-13] In the rest of the paper, only the M_n value resulting from the chain-end titration will be used in calculations because SEC does not allow the discrimination between the acidic and alcoholic chain ends.

The weight fraction of dangling chains can be determined from their molar weight (Table I):

$$w = 45\alpha + (61 + M_D)\beta$$
$$+ (209 + M_D)\theta + (225 + 2M_D)\delta$$

which leads, for instance, to $w = 0.03$ (3%) for sample J and 0.21 (21%) for sample L.

Double Bonds

A number of the maleic double bonds were consumed by side-reactions during the prepolymer polycondensation.[10-13] Using the method of Ordelt,[11] the number so consumed can be determined by ^{13}C NMR, using the peaks at 37 ppm and 75 ppm for saturated carbons and at 131.5 ppm and 134.5 ppm for unsaturated ones (maleate and fumarate).

The results are listed in Table II. It appears that about 5% of the double bonds were saturated for all the samples except C (DEG), for which only 1.5% were lost, and F (PG with a high maleate content), for which the concentration of reacted double bonds was about twice than for the others (9.6%).

The maleate–fumarate isomerization can be studied with proton spectra using the fumarate (6.9 ppm)/maleate (6.2 ppm) intensity ratio, according to Curtis et al.[14] The results listed in Table II show that the isomerization was more than 94% except for C (DEG) and D (NPG) where it was significantly lower.

The solid state spectra (Fig. 2) reveal the absence of significant signal around 114 ppm, which means that the number of residual double bonds in the crosslinked polymers is negligible.

Rubber Elasticity

The measured values of the shear modulus in the rubbery state, G'_r and the calculated values of N,

Table I Codes and Characteristics of Prepolymers, and Theoretical Dangling Chain Concentrations for Samples Studied

Sample	Diol	p	s	I_a ($\times 10^6$)	I_{OH} ($\times 10^6$)	M_n (a)	P	α ($\times 10^6$)	β ($\times 10^6$)	θ ($\times 10^6$)	δ ($\times 10^6$)
B	DPG	0.54	0.42	226	463	1850	4	104	213	122	250
C	DEG	0.54	0.38	175	446	2000	3	81	205	94	241
D	NPG	0.54	0.45	159	249	2700	3	73	115	86	134
A	PG	0.54	0.40	226	410	1400	4	104	189	122	221
E	PG	0.54	0.37	256	446	2100	3	118	205	138	241
H	PG	0.54	0.45	170	73	3680	2	78	34	92	40
J	PG	0.54	0.44	148	41	3870	2	68	19	80	22
K	PG	0.54	0.42	372	267	2700	2	171	123	201	144
L	PG	0.54	0.40	406	713	860	3	187	327	220	384
F	PG	0.30	0.45	210	300	3390	4	147	210	63	90
G	PG	0.54	0.43	210	289	2180	6	97	133	113	156

(a), determined by SEC; p, phthalate molar fraction; s, styrene weight fraction; I_a and I_{OH} respectively, acid and alcohol concentrations in mole/g. M_n, molar weight of the prepolymer, P, polydispersity; α, β, θ, δ, concentration of the various types of chain ends (see text).
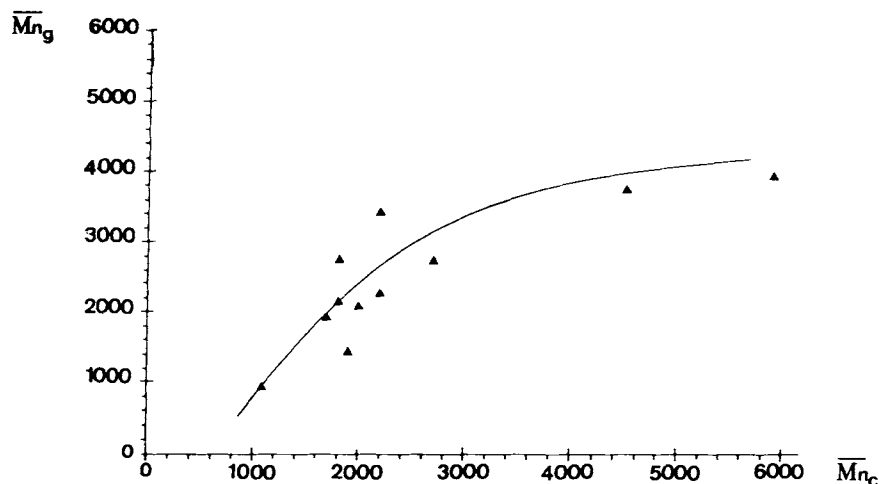
Figure 1 Correlation between prepolymer M_n values determined by steric exclusion chromatography (M_{n_G}) and by chemical titration (M_{n_c}).

M, and M_c according to equations VIII and IX, are listed in Table II. $G'_r/RT\rho$ has been plotted against the theoretical concentration of elastically active subchains M_c^{-1} in Figure 3. These results can be interpreted in at least two ways.

1. The linear dependence between $G'_r/RT\rho$ and M_c^{-1} found in Figure 3 reflects a physical reality. The following relationship can be derived from this figure.

$$G'_r/RT\rho \approx 3 \cdot (M_c^{-1} - 1.5) \tag{11}$$

where M_c^{-1} is expressed in mol/kg.

This leads to the hypothesis that the true concentration of EAS is lower than the theoretical one, the average difference being 1.5 mol/kg^{-1}. The only significant source of difference is the existence of dangling chains due to the styrene/fumarate copolymerization. However, its expected value according to Bergmark and Flodin,[8] [$b_s/2$ as in eq. (3) and (4)], is 0.015–0.50 mol/kg, that is 3 to 10 times lower than the experimental one.

Another argument against the above hypothesis is the fact that, according to eq. (11), the systems B and C would have an especially low crosslink density. However, as it will be seen in the next part of this paper, these systems display an especially high crosslinking effect in the glass transition temperature which would not be consistent with the results derived by application of eq. 11.

2. The linear dependence between $G'_r/RT\rho$ and M_c^{-1} is coincidental, the non-ideality of the networks is expressed by a front factor ϕ

$$G'_r = \phi \cdot RT\rho \cdot M_c^{-1} \tag{12}$$

where ϕ would be about 0.5–0.6 for dimeric diol systems (DEG, DPG), and 0.8–1.7 for

Table II NMR and Elasticity Data for the Networks Under Study

| Sample	% Fum	% Sat	G'_r (MPa)	ρ (g cm^{-3})	G'_r RTP	N	M (g M^{-1})	M_c	T_g (K)
B	94.7	5.1	3.97	1.13	1.085	5.49	2929	534	359
C	85.7	1.5	4.69	1.17	1.258	7.64	3225	422	353
D	79.2	4.7	7.06	1.12	1.852	10.78	4910	456	379
A	96.5	4.8	10.0	1.13	2.515	8.55	3166	370	393
E	96.6	5.7	10.1	1.13	2.516	8.05	2859	355	397
H	98.6	5.5	10.89	1.13	2.725	21.62	8181	378	395
J	95.6	5.8	13.18	1.13	3.291	28.66	10536	368	396
K	97.5	4.9	11.24	1.15	2.813	8.05	3100	385	395
L	97.7	4.3	8.6	1.15	2.145	4.37	1780	407	389
F	96.9	9.6	29.0	1.15	7.032	17.08	4001	235	431
G	94.0	5.5	14.4	1.15	3.644	9.94	3859	388	413

$R = 8.32$ J mol^{-1} K^{-1}.
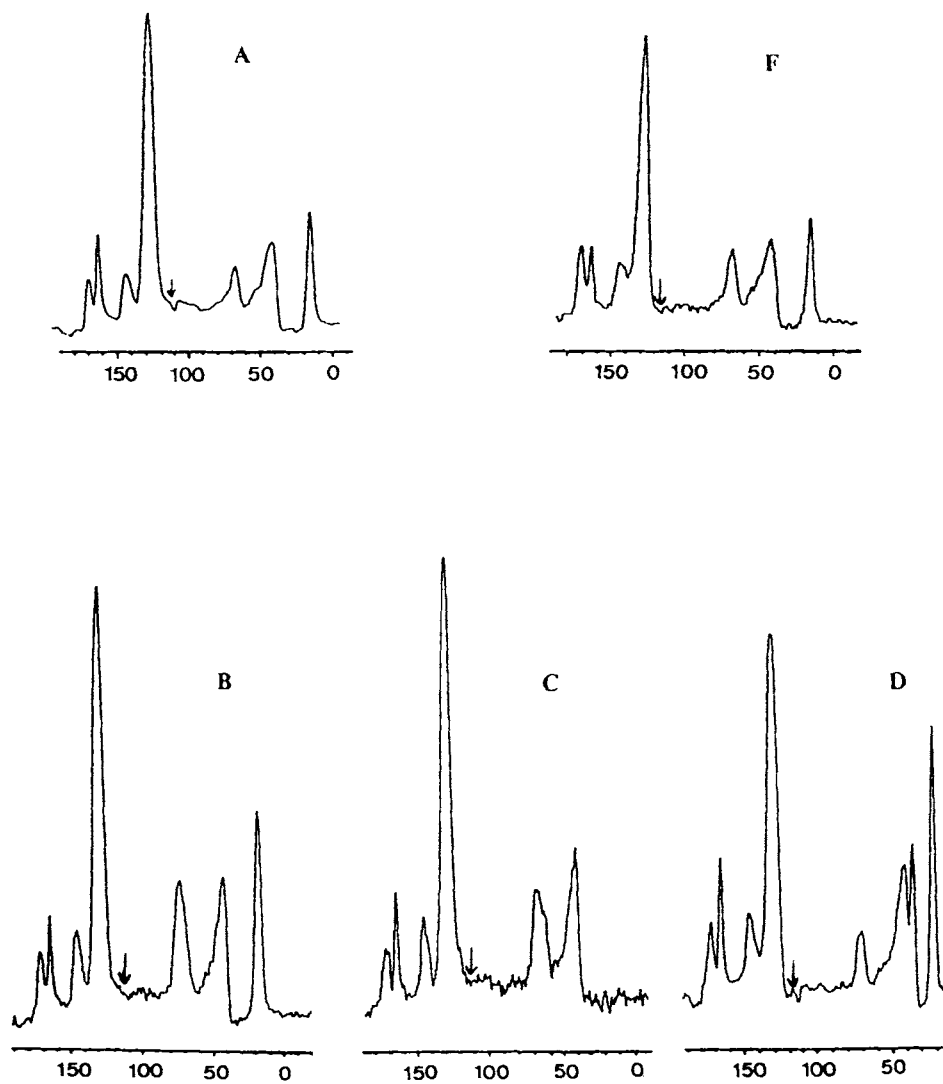
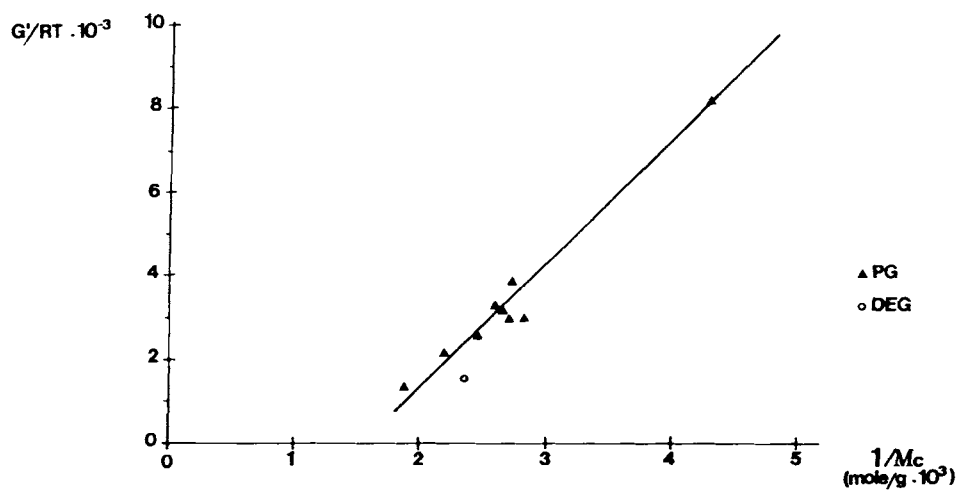**Figure 2** Example of solid state NMR spectrum.

Figure 3 Reduced elastic modulus in rubbery state versus theoretical concentration of elastically active subchains.

PG systems, with a tendency to increase with the crosslink density as previously found.[15,16]

The variations of ϕ with structure are usually interpreted in terms of network statistics (Gaussian character),[17] or steric hindrance effects.[18,19] In the case under study, where two types of network strands, polyester and polystyrene, coexist, the non-ideal character of the network is obvious.

A structural parameter which seems to be interesting is the number of flexible bonds per crosslink. Each crosslink mere is linked to four subchains: two of the polyester type, two of the polystyrene type. The number of flexible bonds per chain is thus:

$$\gamma = \frac{\gamma_s + \gamma_e}{2} \qquad (13)$$

where γ_s and γ_e are the respective numbers of flexible bonds per polystyrene and per polyester subchain.

For a polystyrene subchain:
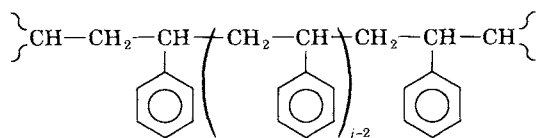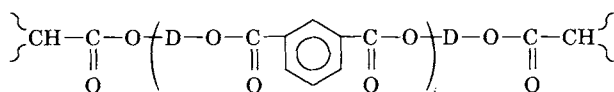

$$\gamma_s = 1 + 2j$$

For a polyester subchain:

Table III   Average Number of Bonds Capable of Rotation in the Polyester Segment γ_e, in the Polystyrene Segment γ_s, and Per Crosslink γ

Sample	γ_e	γ_s	γ	$2n_4 + n_3$[a]	f[b]
B	21.74	8.30	15.02	1.531	0.13
C	21.74	6.46	14.10	2.058	0.05
D	17.39	8.22	12.80	1.991	0.44
A	15.21	6.10	10.65	2.384	0.46
E	15.21	5.50	10.35	—	—
H	15.21	7.26	11.24	—	—
J	15.21	7.00	11.10	2.626	0.58
K	15.21	6.54	10.88	2.228	0.53
L	15.21	6.10	10.68	1.875	0.43
F	10.00	4.84	7.42	4.004	0.67
G	15.21	2.92	9.06	2.316	0.65

[a] Crosslink density according to Grassley.
[b] Non-ideality factor.

where $i = p/(1 - p)$, and D is the diol structural unit which contains γ_D flexible bonds.

$$\gamma_e = (6 + \gamma_D) \cdot (1 + i) \qquad (14)$$

It is interesting to remark that in the case of F ($i = 0.4$) there are essentially two types of polyester subchains with $i = 0$ and $i = 1$, respectively.

In the case of the other systems ($i = 1.17$), there is probably a large predominance of subchains having $i = 1$, according to the previously made hypothesis of alternating of phthalate and maleate structure units.

The values of γ determined from the above equations are listed in Table III.

Cook[15] states that the steric hindrance as well as the non-Gaussian character effects can be represented by a factor f such that:

$$G'_r = \frac{0.5}{1 - f} \cdot RT\rho \cdot M_c^{-1} \qquad (15)$$

where f can take various expressions depending on the chosen theory.[17-19] The values of f are listed in Table III and plotted against γ in Figure 4. As expected, f is a decreasing function of the number of flexible bonds between crosslinks. The samples B and C based on dimeric diols are close to ideal networks ($f \simeq 0$), whereas the departure from ideality increases with the crosslink density.

In the case of the tetrahydrophthalate system (G), the experimental value of the rubbery modulus is noticeably higher than for homologue phthalate systems, for instance A. As a consequence, the representative point of G is far away from the average curve in Figure 4. It can be hypothesized in this case that the true crosslink density is higher than the theoretical one because tetrahydrophthalate (THP) double bonds participated in the radical copolymerization.
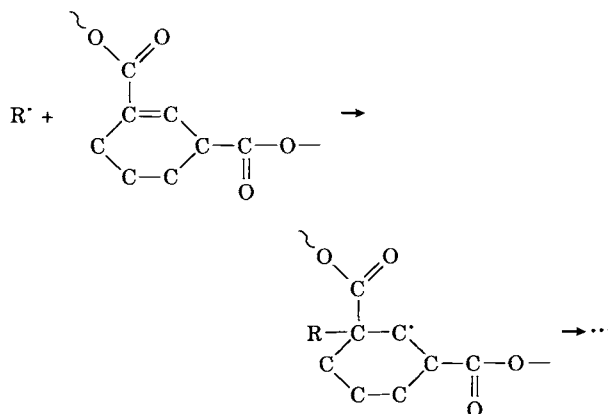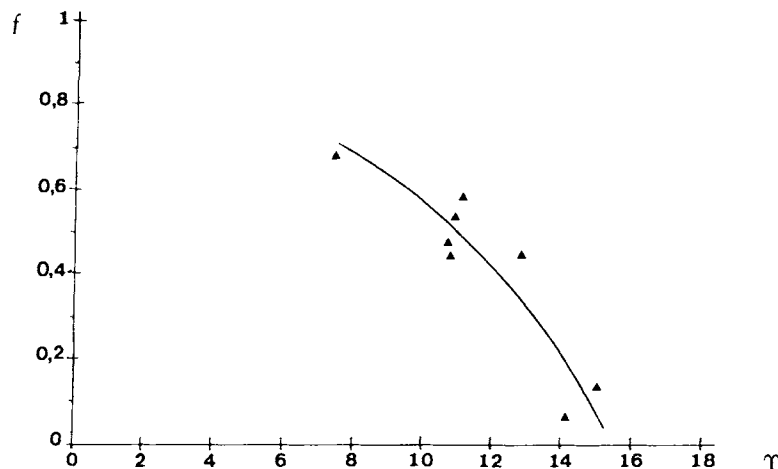
Figure 4 Non-ideality factor, according to rubber elasticity theory, versus average number of flexible bonds between crosslinks.

Radical crosslinking by addition to the THP double bond was recently found in a study of the thermal oxidation of epoxies cured by the tetrahydrophthalic anhydride.[20]

The important role of dangling chains appears clearly in the series J, K, L. For the study of this peculiar point, it is interesting to distinguish the "tri" and "tetrafunctional" crosslinks and to use Graessley's formula[21] used by Cook.[15] In the case of polyesters

$$G_r' = \phi' \cdot RT\rho \cdot (2n_4 + n_3) \qquad (16)$$

where n_4 and n_3 were previously determined.

The new front factor ϕ' was determined according to eq. (16). It undergoes the same variations as ϕ with the structure, except for the effect of dangling chains (systems J, K, L), for which it is practically constant ($\phi' = 1.20 \pm 0.05$) whereas it was an increasing function of the crosslink density in the preceding formulation (Table III).

From an empirical view point, it can be remarked that G_r' is a practically linear function of the chain ends concentration b (Fig. 5).

$$G_r' = 14 - 5.10^{-3}b \qquad (17)$$

where G_r' is expressed in MPa and b in μmol g^{-1}.

This relationship is especially useful in degradation studies where each chain scisson creates two new polyester chain ends.
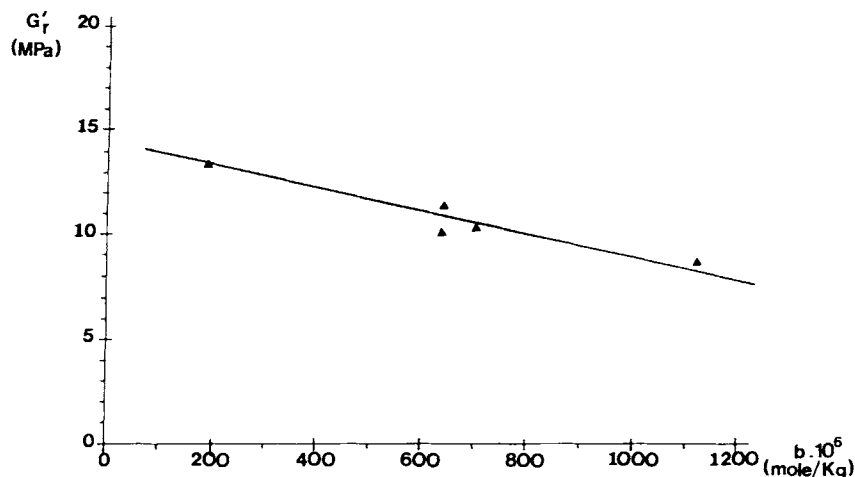

Figure 5 Rubber elastic modulus versus polyester dangling chain concentration for the sample family based on propylene glycol, with phthalate molar fraction $p = 0.54$.

CONCLUSIONS

We have attempted to give as precise a description as possible of the network structure for the ten styrene crosslinked polyesters under study.

From IR and NMR measurements, it appears that, for the chosen cure conditions, less than 10% of the initially present maleic double bonds are unreacted or lost in side reactions. Some of these latter lead to trifunctional crosslinks (by addition of chain end alcohols). The main network structural irregularities are essentially dangling chains corresponding to prepolymer chain ends and to species resulting from interruption processes of the styrene/fumarate copolymer growth. The hierarchy of rubbery modulus values suggests that the former predominates largely over the latter type.

The weight fraction of dangling chains can be estimated. It is in the range of 5% to 20% for the majority of the samples.

From the experimental values of the front factor ϕ, a "non-ideality" factor f, expressing the departure from the classical rubber elasticity theory, can be determined. The value of f increases when the number γ of flexible bonds between crosslinks decreases, which can result from the non-Gaussian character of the networks or the steric hindrance effects inherent to high crosslink densities.

In the case of tetrahydrophthalate systems, the experimental data are consistent with the hypothesis of crosslinking side reactions at the THP double bond level.

Concerning the role of prepolymer chain length, the following results were obtained:

1. The results are in reasonable agreement with Graessley's approach of the rubber elasticity in networks having crosslinks of various functionalities. Since chain ends resulting from the interruption of the styrene–fumarate copolymerization have been neglected in the calculation of n_3 and n_4, it can be concluded that their contribution to n_3 is probably negligible.
2. The rubbery modulus appears as a linear decreasing function of the chain-end concentration.

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