Structure–Property Relationships for Styrene Crosslinked Polyesters. II. Glass Transition Temperature

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SYNOPSIS

The glass transition temperature of 10 styrene-free polyester prepolymers and the corresponding networks crosslinked by about 40% by weight of styrene were determined by DSC (and by DMA in the case of networks).

The glass transition temperature T_{g_L} of an hypothetical copolymer containing all the difunctional units of the network was then calculated. It is an increasing function of the molar weight of the prepolymer and of the phthalate/maleate molar ratio. From IR and NMR measurements, it was established that the structural irregularities other than polyester chain ends, especially unreacted double bonds, can be neglected to a first approximation. A constituent repeat unit (CRU) defined on the basis of these results allows the calculation of the crosslink density n. Then, various theories of the effect of n on T_g are compared. It appears that neither the Fox and Loshaek nor the Di Marzio approach gives good results. The crosslinking constants are lower than those found for aliphatic skeleton polyesters or epoxies. In the series under study, they display a tendency to decrease with the aromatic content. Some possible reasons of this peculiar behavior are discussed.

INTRODUCTION

There is now a great scientific and technological interest in the structure–property relationships in the field of thermosets used as composite matrices. Indeed, the glass transition temperature T_g is one of the most important properties, which justifies the relative abundance of the literature on its prediction methods.[1-5]

For the majority of these methods, at least two important characteristics are needed: T_{g_L}, the glass transition temperature of an hypothetical linear copolymer containing all the difunctional groups of the network, and n, the crosslink density. When the polymer contains various types of crosslinks, methods have been proposed to take into account their different characteristics.[4-6]

In the typical case of rubber vulcanization where the starting material is made of large chains and where the crosslink density is low, the copolymer effect of crosslinking, for instance the local change of structure of difunctional groups induced by crosslinking, can be neglected, so that T_{g_L} is the experimental value of the glass transition temperature of the prepolymer. For high values of the crosslink density, however, the copolymer effect of crosslinks cannot be neglected. In the case of a crosslinking by addition to prepolymer double bonds, for instance:
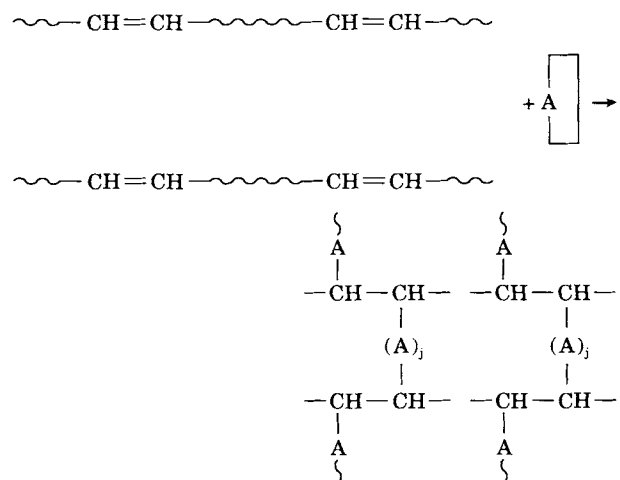
The double bond, which contributed to the copolymer effect in the starting prepolymer, disappears in the network. This latter, in contrast, contains the group—A— which was not present in the prepolymer. The T_g of this latter cannot therefore be assimilated to the network's T_{g_L}. In this case, T_{g_L} must be calculated using the various relationships available for T_g prediction in copolymers.[7-10]

The crosslink effect can be expressed through various expressions derived from the theories of free volume,[1] entropy,[2] or more or less empirical considerations.[3]

In the case of amine cured epoxies, it appeared that:

1. $M_i \cdot T_{g_i}^{-1}$ is an additive function useful for T_{g_L} calculations.[4]
2. The glass transition temperature T_g of the network can be calculated by the Di Marzio's relationship:[2]

$$T_g = T_{g_L}(1 - K_{DM} \cdot F \cdot n)$$

where K is a universal constant ($K_{DM} \approx 3$ for trifunctional crosslinks), n is the crosslink density, and F is a flex parameter increasing with the segment stiffness, for instance, generally with T_{g_L}.[4]

In the case of unsaturated polyesters crosslinked by a monomer, it was found that T_g is an increasing function of the crosslink density,[11,12] whose influence can be relatively well represented by Di Marzio's relationship.[2] These studies were focused on poly-
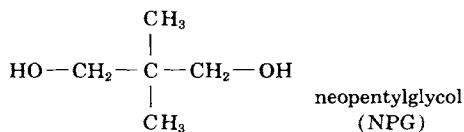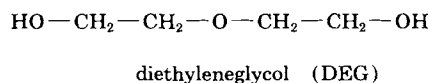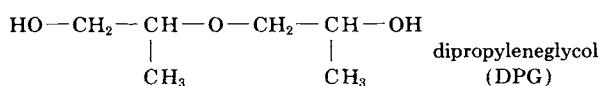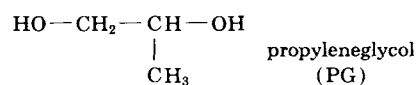
esters having an aliphatic skeleton and, generally, a low T_g value.

The aim of the present work is to try to apply the above approaches to T_g predictions for a series of polyester networks used in composite applications and containing phthalic esters whose role is, in principle, to increase the chain stiffness.

EXPERIMENTAL

Materials

The polyesters were comaleate/phthalates of various diols HO — D — OH whose structure and designating code are shown below:

$$HO—CH_2—\underset{\underset{CH_3}{|}}{CH}—OH \qquad \text{propyleneglycol (PG)}$$

$$HO—CH_2—\underset{\underset{CH_3}{|}}{CH}—O—CH_2—\underset{\underset{CH_3}{|}}{CH}—OH \qquad \text{dipropyleneglycol (DPG)}$$

$$HO—CH_2—CH_2—O—CH_2—CH_2—OH$$

diethyleneglycol (DEG)

$$HO—CH_2—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—OH \qquad \text{neopentylglycol (NPG)}$$

The phthalate/maleate molar ratio $p/(1 - p)$

Table I Code and Characteristics of the Systems Under Study

Sample	Diol	$p/(1 - p)$	s	q	j	I_a ($\times 10^6$)	I_{OH} ($\times 10^6$)	M_n	M
A	PG	0.54/0.46	0.40	10.38	2.55	226	410	1900	3170
B	DPG	0.54/0.46	0.42	7.05	3.65	226	463	1700	2930
C	DEG	0.54/0.46	0.38	9.39	2.73	175	446	2000	3230
D	NPG	0.54/0.46	0.45	12.80	3.61	159	249	2700	4910
E	PG	0.54/0.46	0.37	9.84	2.25	256	446	1800	2860
F	PG	0.30/0.70	0.45	12.87	1.92	210	300	2200	4000
G	PG	0.54/0.46	0.43	11.89	2.92	210	289	2200	3860
J	PG	0.54/0.46	0.44	32.24	3.00	148	41	5900	10540
K	PG	0.54/0.46	0.42	9.29	2.77	372	267	1800	3100
L	PG	0.54/0.46	0.40	5.74	2.55	406	713	1050	1750

Abbreviations: $p/(1 - p)$, phthalate/maleate molar ratio; s, styrene weight fraction; q, number of diol units in a prepolymer chain; j, number of styrene units per maleate double bond; I_a and I_{OH}, concentration of acidic and alcoholic chain ends in μmol g^{-1}; M_n, number average molecular weight of the prepolymer (g mol^{-1}), determined from I_a and I_{OH} values. M, molar weight of the CRU (g mol^{-1}).

was 0.30/0.70 for sample F and 0.54/0.46 for all the other samples.

The cure conditions and presumed structure were described in the first part of this article. Some of their important characteristics are summarized in Table I. I_a and I_{OH} are the respective acidic and alcoholic chain-end concentrations in the prepolymer mixture. The styrene-free prepolymers were obtained by distillation in vacuo of the reactive mixture. They contained less than 1% residual styrene as checked by FTIR spectrophotometry.

T_g Measurements

Two methods were used to determine the glass transition temperature:

1. Differential scanning calorimetry (DSC), using the Perkin Elmer DSC 2 apparatus at 20 K min^{-1}. T_g was taken at the inflexion point.
2. Measurement of viscoelasticity using the Brabender viscoelastometer at 5 Hz. In this case, T_g was taken at the maximum of tan δ.

As expected,[13] this latter value is 6–20 K higher than the former one. Viscoelastic measurements were made only on networks, whereas DSC measurements were made on both prepolymers and networks. All the calculations are made on the basis of DSC data. The T_g values obtained by this latter method vary noticeably from one sample to another one and, for a given sample, from a location to another one. The maximum amplitude of these variations is typically $\Delta T_g \simeq 20$ K. The maximum value was taken for the calculations.

CALCULATIONS

The Constitutive Repeat Unit (CRU)

As in the first part of this paper, the chosen CRU will be based on a single chain of the starting prepolymer:
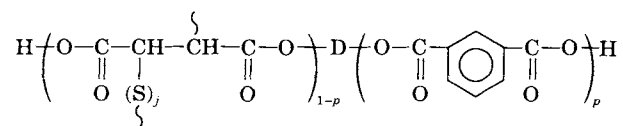
Its molar mass is M such that $M = \dfrac{M_n}{(1 - s)}$, M_n being the number average molar mass of the pre-

polymer and s the styrene weight fraction. The chain ends resulting from the styrene/maleate copolymerization and the prepolymer structural irregularities (except chain ends), will be neglected. The number of styrene units per maleic units is:

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

The CRU contains thus M_n grams of polyester and $(M - M_n)$ grams of styrene monomer units. The M_n grams of polyester are composed of:

q diol structural units $-D-$,

$2q$ $-\underset{\underset{O}{\|}}{C}-O-$ ester units and,

p·q isophthalic rings
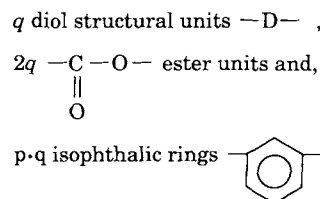
The maleic/fumaric double bonds have disappeared, they are transformed into crosslinks of two types:

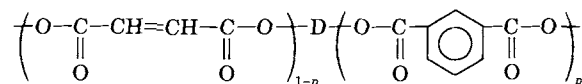| tetrafunctional crosslink | trifunctional crosslink | B = chain end |
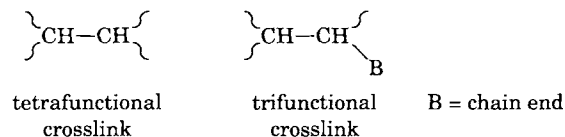
Each CRU contains two "trifunctional" and $q \cdot (1 - p) - 2$ "tetrafunctional" crosslinks.

The whole crosslink density is:

$$n = q \cdot \frac{(1 - p)}{M} = n_3 + n_4 \qquad (2)$$

where $n_3 = \dfrac{2}{M}$ and $n_4 = \dfrac{q \cdot (1 - p) - 2}{M} \qquad (3)$

Concerning the prepolymer, the simplest repeat unit (SRU) would be:

Effect of Chain Ends on the Glass Transition Temperature of the Prepolymer

The chosen additive law for the copolymer effect, can be ascribed, in the case of prepolymer:

$$\frac{M_P}{T_{gP}} = \frac{M_P}{T_{g\infty}} + 2b \qquad (4)$$

where M_P is the M_n of the prepolymer whose T_g (experimental value in Table II) is T_{gP}; $T_{g\infty}$ is the T_g of a chain of same structure but infinite length; $2b$ is the contribution of both chain ends to $M \cdot T_g^{-1}$.

It was already observed that this relationship is equivalent to the Fox and Flory law[14] on the $(T_g - M_n)$ relationship.[4]

Equation (4) can be rewritten:

$$\frac{1}{T_{gP}} = \frac{1}{T_{g\infty}} + \frac{2b}{M_P} \tag{5}$$

For the five PG systems based on the same SRU $(p/(1-p) = 0.54/0.46)$, that is, A, E, J, K, and L, T_{gP}^{-1} was plotted against M_n^{-1} in Figure 1. The resulting curve can be represented by the equation:

$$T_{gP}^{-1} = 3.03 \times 10^{-3} - 0.155 \cdot M_n^{-1}$$

Thus $T_{g\infty} = 330$ K and $2b = 0.155$

Contribution of Maleic/Fumaric Double Bonds to the "Copolymer Effect"

Let us consider the SRU of PG samples for which respectively $p/(1-p) = 0.54/0.46$ and $p/(1-p) = 0.30/0.70$. For a linear infinite chain, it can be written:

$$\frac{M_{\text{SRU}}}{T_{g\infty}} = \frac{M_{C\theta0}}{T_{gC\theta0}} + \frac{M_D}{T_{gD}} + p \cdot \frac{M_{PH}}{T_{gPH}} + (1-p) \cdot \frac{M_M}{T_{gM}} \tag{6}$$

where: $M_{C\theta0} = 88$ g mol^{-1}, $M_D = 42$ g mol^{-1}, $M_{PH} = 76$ g mol^{-1} and $M_M = 26$ g mol$^-$, the indices

PH and M referring to the ⬡ and —CH = CH— structural units, respectively.

In the case of (0.54/0.46) systems $T_{g\infty} = 330$ K.

In the case of (0.30/0.70) systems (F), $T_{g\infty}$ can be calculated from eq. (5), making the hypothesis that b is almost independent of the prepolymer structure (in this structural series) and that $2b = 0.155$. The calculation gives $T_{g\infty F} = 316$ K.

The system of eq. (6) applied to the (0.54/0.46) and to the (0.30/0.70) systems can be now resolved:

$$\frac{183}{330} = \frac{88}{T_{gC\theta0}} + \frac{M_D}{T_{gD}} + 0.54 \cdot \frac{76}{T_{gPH}} + 0.46 \cdot \frac{26}{T_{gM}} \tag{7a}$$

$$\frac{171}{316} = \frac{88}{T_{gC\theta0}} + \frac{M_D}{T_{gD}} + 0.30 \cdot \frac{76}{T_{gPH}} + 0.70 \cdot \frac{26}{T_{gM}} \tag{7b}$$

Since $T_{gPH} = 432$ K,[4] it follows that $T_{gM} = 216$ K.

The contribution of the difunctional units of the polyester (excluding maleate ones), can thus be written:

$$\frac{M_{LP}}{T_{gLP}} = \frac{M_P - 26 \cdot q(1-p)}{T_{gLP}}$$

$$= \frac{M_P}{T_{gP}} - 26 \cdot \frac{q(1-p)}{T_{gM}} \tag{7}$$

Copolymer Effect

For the chosen CRU, the copolymer effect can be written:

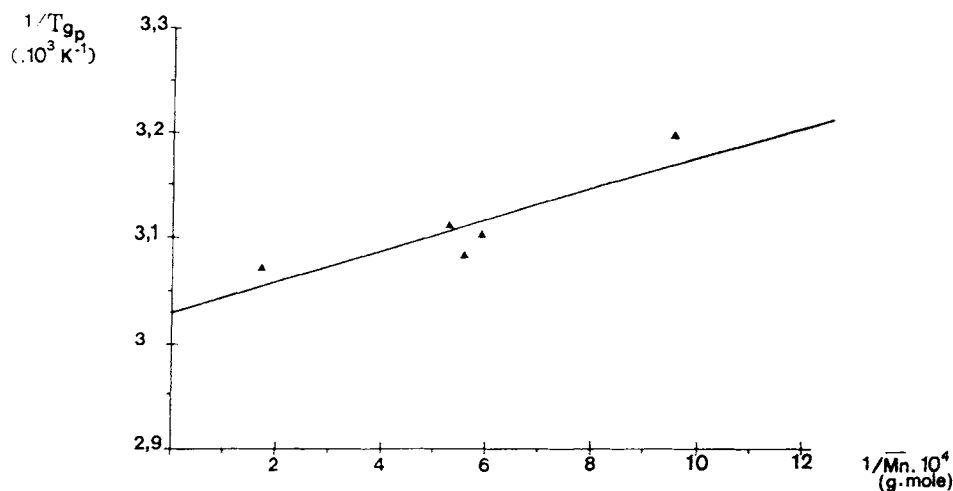$$\frac{M_L}{T_{gL}} = \frac{M_{LP}}{T_{gLP}} + \frac{M_S}{T_{gS}} \tag{8}$$

Figure 1 Fox and Flory plot for the polyester prepolymers.

where $M_L = M - 26 \cdot q(1 - p)$ is the mass of the totality of difunctional units of the network, $M_{LP}/T_{g_{LP}}$ is the contribution of polyester groups and $M_S T_{g_S}$ is the contribution of styrene monomer units, M_S being the styrene mass in the CRU ($M_S = s \cdot M$) and T_{g_S} the T_g of a polystyrene of infinite molar weight $T_{g_S} = 370$ K. The above equations allow the calculation of T_{g_L}.

Crosslinking Effect

Two relationships were tested:

$$T_g = T_{g_L}/(1 - K_{DM} \cdot F \cdot n)$$

as proposed by Di Marzio[2]

$$T_g = T_{g_L} + K_{FL} \cdot n$$

as proposed by Fox and Loshaek[1]

In the Di Marzio's relationship, F is the flex parameter which can be determined as follows:

1. For a given segment i, $F_i = m_i/\gamma_i$ where m_i is the molar mass of the segment which contains γ_i skeletal bonds capable of rotation.[2] For a given crosslink linked to k chains:[4]
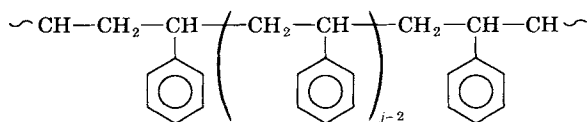
$$F = \frac{1}{k} \cdot \sum_k F_i$$

2. In the case of polyesters, each crosslink is connected to four segments, two of the polyester type and two of the polystyrene type, thus:

$$F = \frac{1}{2} \cdot (F_i + F_2)$$

where the indices 1 and 2 refer respectively to the polystyrene and polyester segments.
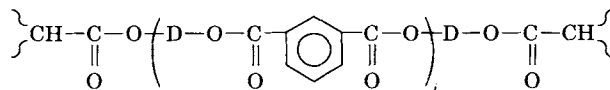
3. For the polystyrene segment:

$$\sim CH-CH_2-CH \left(CH_2-CH \right)_{j-2} CH_2-CH-CH \sim$$

The flex parameter is given by

$$F_i = \frac{104 \cdot j}{1 + 2j}$$

where j has just been previously defined.

4. It was supposed that the average polyester segment is for the type:

$$\left[CH-C-O \left(D-O-C \underset{\text{(ring)}}{\bigcirc} C-O \right)_i D-O-C-CH \right]$$

where $i = p/(1 - p)$ and $\gamma_e = (6 + \gamma_D) \cdot (1 + i)$ where γ_D is the number of "inner" rotatable bonds in the diol unit: $\gamma_D = 1$ (PG), 2 (NPG), or 4 (DEG and DPG).

The flex parameter is thus:

$$F_2 = \frac{88 + M_D + (164 + M_D)i}{(6 + \gamma_D) \cdot (1 + i)}$$

The corresponding values of F are listed in Table II.

RESULTS AND DISCUSSION

The measured values of the glass transition temperatures of prepolymers and networks under study are reported in Table II, where the calculated data relative to the copolymer (T_{g_L}) and crosslinking effect on T_g are also listed. T_{g_P}, T_{g_L}, and T_g are plotted in Figure 2 against sample code. These results call for the following comments:

(a) T_{g_L} is higher than T_{g_P} as a result of the high stiffness of polystyrene segments whose

Table II   Glass Transition Temperature: Experimental Results and Calculated Data

Sample	T_{g_P} (DSC) K	T_g (DSC) K	T_g (TMA) K	T_{g_L} K	n (theo) mol/kg	n (exp) mol/kg
A	322	388	393	348	1.508	1.246
B	288	358	359	322	1.107	0.538
C	273	348	353	308	1.379	0.624
D	300	380	379	340	1.199	0.931
E	325	388	397	349	1.584	—
F	309	428	431	346	2.251	3.259
G	298	374	383	332	1.417	1.841
J	326	388	396	352	1.408	1.631
K	323	387	395	349	1.458	1.394
L	313	375	389	349	1.508	1.082

Abbreviations: T_{g_P}, T_g of the prepolymer determined by DSC; T_g (DSC), T_g of the network determined by DSC (maximum value); T_g (TMA), T_g of the network determined by thermomechanical analysis; T_{g_L}, calculated value (see text); n (theor) and n (exp), crosslink densities from calculation for the chosen CRU and rubber elasticity measurements, respectively.
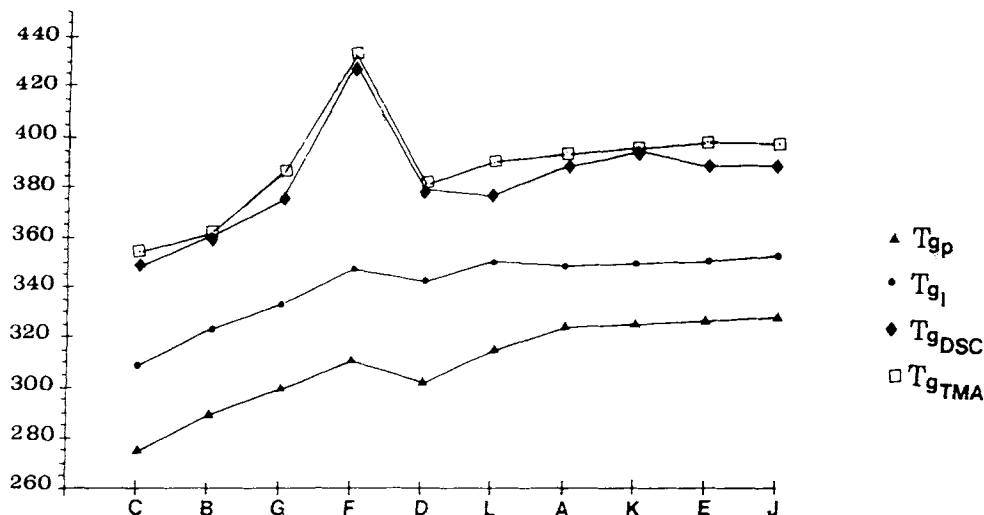
Figure 2 T_g values versus sample code. Remark: average value for T_g determined by DSC.

contribution to T_{gL} ($T_{gS} = 380$ K) is especially high compared to the contributions of the other groups.

(b) T_{gL} varies in the same way as T_{gP} as a result of the constancy of the styrene weight fraction ($s = 41\% \pm 4\%$).

(c) The "softening" effect of double bonds appears clearly in the glass transition temperatures of the prepolymers: T_{gP} increases by 13–16 K when the maleate molar fraction varies from 0.70 (F) to 0.46 (A or E). It would be therefore incorrect to assimilate T_{gP} into the contribution of polyester chains to T_{gL}, since double bonds are lacking in the network where they have been transformed into crosslinks.

(d) As expected from molecular stiffness considerations, T_{gL} is lower for tetrahydrophthalate (G) than for homologue phthalate (A, E, $\cdots$) systems.

In the same way, the fact that $T_{gL}(\mathrm{C})$ < $T_{gL}(\mathrm{B})$ and $T_{gL}(\mathrm{D})$ < $T_{gL}(\mathrm{A})$ agrees with the experimental data obtained on T_g of hydrocarbon polymers: $T_g(\mathrm{PE})$ < $T_g(\mathrm{PP})$ and $T_g(\mathrm{PiB})$ < $T_g(\mathrm{PP})$.[7]

(e) The crosslinking effect appears also clearly in Figure 2 where ($T_g - T_{gL}$) is considerably higher for the maleate-rich sample F than for all the others.

(f) ($T_g - T_{gL}$) appears also significantly higher for the tetrahydrophthalate system (G) than for the phthalate ones of similar maleate

Table III Di Marzio's and Fox and Loshaek's Calculated Parameters

Sample	$K_{DM} \cdot F \cdot n$ ($\times 10^3$)	F ($\times 10^3$) g/mol	K_{DM}	K_{FL} K mol/g	($K_{DM} \cdot F_{exp}$) g/mol	$[\phi]$ ($\times 10^3$) mol/g
A	103.09	33.96	2.01	26.53	83	1.77
B	100.55	34.31	2.65	32.52	187	1.30
C	114.94	32.03	2.60	29.00	184	1.57
D	105.26	35.28	2.49	33.36	113	1.41
E	100.51	33.49	1.89	24.62	—	1.86
F	191.59	31.52	2.70	36.43	59	0.97
G	112.30	34.42	2.30	29.64	61	—
J	92.78	34.51	1.91	25.57	57	1.65
K	98.19	34.24	1.97	26.06	70	1.71
L	69.33	33.86	1.35	17.24	64	1.77

Abbreviations: $K_{DM} \cdot F \cdot n$, "crosslinking term" of the Di Marzio's theory calculated from T_g and T_{gL}; F, calculated flex parameter; K_{DM}, Di Marzio's constant determined from T_g, T_{gL}, F and n (theor); K_{FL}, Fox and Loshaek's constant; ($K_{DM} \cdot F$) theor, determined from T_g, T_{gL} and n (theor); ϕ, phthalate group concentration.

concentration (A, E, · · ·). From a study of the oxidative crosslinking in epoxies cured by tetrahydrophthalic anhydride, it appears that the cyclohexene double bond can be involved in radical crosslinking.[15] In other words, the crosslink density could be higher than its theoretical value in system G.

(g) The constants K_{DM} and K_{FL} of the respective equations of Di Marzio[2] and Fox and Loshaek[1] were determined from T_g and T_{gL} and listed in Table III. They vary in the same way as a result of the quasi constancy of the flex parameter and T_{gL} in the series under study. As a matter of fact, considering that $K_{DM} \cdot F \cdot n \ll 1$:

$$T_g = \frac{T_{gL}}{1 - K_{DM} \cdot F \cdot n}$$

$$\approx T_{gL} + T_{gL} \cdot K_{DM} \cdot F \cdot n \simeq K_{FL} \cdot n$$

In other words, the Fox and Loshaek and Di Marzio relationships are almost equivalent in structural series where T_{gL} and F vary only slightly from one sample to another one.

(h) The above constants were determined using the theoretical values of the crosslink density n. Assuming their validity, it could be concluded that K_{DM} is lower for the polyesters under study than for expoxies,[4] for which it appeared as an "universal" constant $K_{DM} \simeq 3$ and, in principle, $K_{DM} \simeq 6$ for tetrafunctional crosslinks.[2]

Indeed, the first explanation which comes in mind is that the actual crosslink density is far below its theoretical value as a result of the presence of polystyrene chain ends,[16] intramolecular cyclization[17] and other structural irregularities.[18,19] It appeared interesting, thus, to plot $K_{DM} \cdot F \cdot n$ (which represents the crosslinking effect in the Di Marzio's theory), against the reduced rubbery modulus $G'_r/RT\rho$, which is, for an ideal network, proportional to the concentration of elastically active subchains EAS:

$$\frac{G'}{RT\rho} = [EAS] = M_c^{-1} = 2 \cdot n_{exp}$$

in the case of tetrafunctional crosslinks.

The results (Fig. 3) are not less surprising than the preceding ones: For the majority of the samples, $K_{DM} \cdot F \cdot n$ appears as a decreasing function of the experimental value of the crosslink density, except when the structural variable is the concentration of maleate groups in the chain as shown by a comparison of A and F.

Concerning the series of variable prepolymer length (A, E, J, K, and L), the above observations can be reformulated as follows: the dangling chain ends have a considerably lower influence on T_g than on rubbery modulus, which seems to be consistent with recent observations made on non-stoichiometric epoxide-amine networks.[20]

Cook finds values of the product $K_{DM} \cdot F$ in the range (120–160 g/mol).[12] In our case, $K_{DM} \cdot F$ varies between 40 g/mol and 80 g/mol. The difference be-
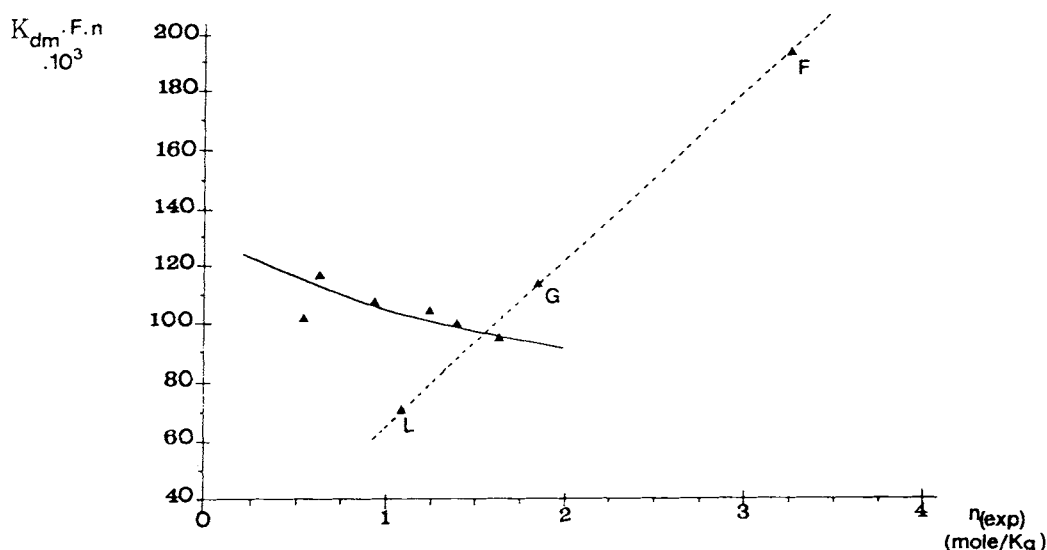

Figure 3 $K_{DM} \cdot F \cdot n$ (from the Di Marzio's equation), versus the experimental value of the crosslink density (determined from rubber elasticity measurements).
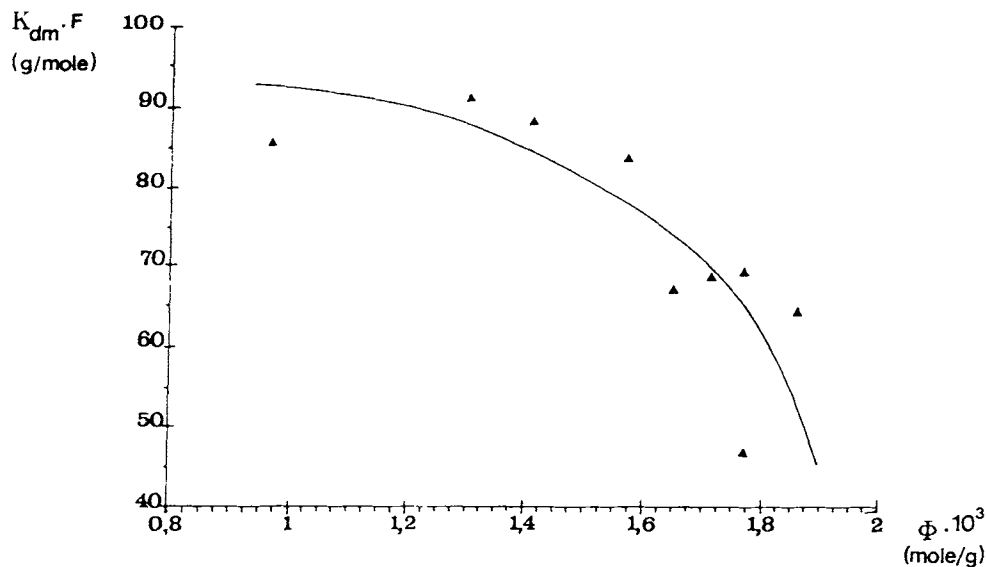
Figure 4 $K_{DM} \cdot F$ (theoretical value) against phthalate concentration.

tween both series is essentially due to the presence, in our case, of phthalate groups in polyester chains, whereas Cook studied only aliphatic skeletal systems with diethylene glycol as diol. In Figure 4, $K_{DM} \cdot F$, determined from the theoretical value of n, was plotted against the phthalate group concentration. The tendency of $K_{DM} \cdot F$ to decrease with the phthalate-concentration seems to be confirmed but remains unexplained since, in principle, aromatic groups increase F and therefore $K_{DM} \cdot F$. It appears thus that the polyesters differ considerably from amine crosslinked epoxies for which Di Marzio's approach gave good predictions. The mean reasons for this "abnormal" behavior of the polyesters could be linked to the following points:

(i) The so-called crosslink mers can eventually participate to entropy changes by a rotation around the carbon–carbon bond

S = polystyrene subchain   E = polyester subchain
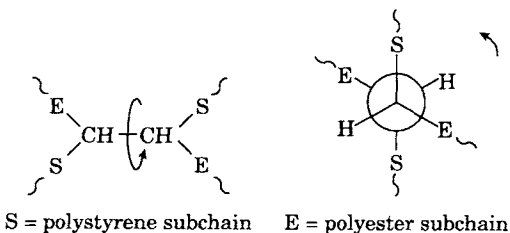
This characteristic is not taken into account in the calculations. It could be imagined that its contribution to cooperative mobility is negligible in the case of flexible subchains, but becomes significant in the case of stiff

subchains, and this seems to be consistent with the experimental results.

(ii) Our network model involves the systematic alternation of fumarate units and styrene subchains. In fact, there is a finite probability of obtaining furmarate dimers.[12]
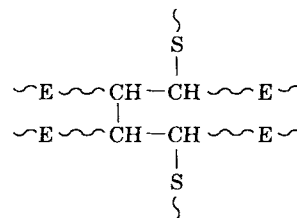
These structural units would act as "hexafunctional" crosslinks whose contribution to T_g is presumably higher than the one of tri- or tetrafunctional crosslinks.[12,21] In the series under study, where the concentration of styrene is almost constant, the concentration of these units must be higher for the maleate-rich sample F than for all the others. This can explain the fact that K_{DM} is considerably higher for F than for the other samples based on the same diol (A, E, J, K, L).

CONCLUSIONS

A method has been proposed for the determination of T_{gL} expressing the "copolymer effect" of the linear segments of polyester networks. For the systems

under study based on close styrene weight fractions, T_{g_L} varies in the same way as T_{g_P} (T_g of the polyester prepolymer): $T_{g_L} - T_{g_P} \simeq 20\text{–}40$ K.

The difference between T_g of the network and T_{g_L} is also nearly constant; $T_g - T_{g_L} \simeq 40$ K, except for the system of high maleate content (F), for which $T_g - T_{g_L} = 85$ K. Thus, Di Marzio's and Fox and Loshaek's models for the crosslinking effect on T_g cannot be applied here since the corresponding constants vary in an opposite way to the one expected, that is, they are decreasing functions of the segment stiffness. This behavior could be explained by some peculiarities of the polyester crosslinks.

REFERENCES

1. T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
2. E. A. Di Marzio, *J. Res. Nat. Bur. Stands.*, **68A**, 611 (1964).
3. A. J. Chompf, *Polymer Networks*, A. J. Chompf and S. Newman, Eds. Plenum, New York, 1971, p. 145.
4. V. Bellenger, E. Morel and J. Verdu, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 1219 (1987).
5. A. J. Di Benedetto, *J. Polym. Sci., Polym. Phys. Ed.*, **B25**, 1949 (1987).
6. V. Bellenger, E. Morel and J. Verdu, *J. Mat. Sci.*, **23**, 4244 (1988).
7. D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymers. Their Correlation with Chemical Structure*, Elsevier, Amsterdam, 1976.
8. W. A. Lee, *J. Polym. Sci.*, **A2**, (8) 555 (1970).
9. E. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).
10. P. R. Couchman, *Macromolecules*, **11**, 1156 (1978).
11. K. Shibayama and Y. Suzuki, *J. Polym. Sci.*, **A3**, 2637 (1965).
12. W. D. Cook, *Eur. Polym. J.*, **14**, 713 (1978).
13. G. Lee and B. Hartmann, *J. Appl. Polym. Sci.*, **29**, 1471 (1984).
14. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).
15. M. Lehuy, Thesis, ENSAM, Paris, 1990.
16. P. Bergmark and F. Flodin, *Composite Systems from Natural and Synthetic Polymers*, Lsalmen, A. De Ruvo, J. C. Seferis, and E. B. Stark, Eds. Elsevier, Amsterdam, 1986.
17. Y. S. Yang and S. L. Lee, *Polymer*, **29**, 1793 (1988).
18. Z. Ordelt, *Makromol. Chem.*, **63**, 152; **68**, 166 (1963).
19. D. Judas, A. Fradet, and E. Marechal, *Makromol. Chem.*, **185**, 2583–2597 (1984).
20. V. Bellenger, W. Dhaoui, J. Verdu, J. Galy, Y. G. Won, and J. P. Pascault, *Polymer*, **30**, 2013 (1989).
21. F. Rietsch, D. Daveloose, and D. Froelich, *Polymer*, **17**, 859 (1976).