

On The Correlation of Some Theoretical and Experimental Parameters in Polycondensation Cross-linked Networks

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ABSTRACT: The use of the equation $f = km/\alpha E$, correlating number of degrees of freedom m of polymer segments between cross-linking nodes in polycondensation networks to the energy of interaction polymer segment/polymer segment, both within the same polymer and at different polymers interfaces, through measures of deflection in bending by dynamic thermomechanical analysis, yields a number of consequences of interest in the field of polycondensation-hardened networks and of their process of hardening. From this equation, regression equations correlating only two parameters are obtained, which render easier the determination of the parameters that are more difficult or lengthy to obtain by experimental means. The process of networking, hence of the reaction of polycondensation between the gel point and complete hardening of the network, can be followed by the determination of the average number of degrees of freedom m of the polymer segments between cross-linking nodes obtained through these equations. Even the equation of Carothers can be adapted through the use of the average number of degrees of freedom of polymer segments between cross-linking nodes to describe the course of the polycondensation after the gel point and up to complete stable networking. The dependence from the temperature of m can be connected to both the rate constant of advancement of the network and to the correlation of the value of m of the system to its glass transition temperature. Peculiarities in gel point forecasting by Flory's and Carothers' theories, which depend on the well-known existence of reactions of cyclization during polycondensation and by a thermodynamic temperature dependence not previously recognized, indicate that the gel point predicted by each theory fails to consider the existence of one and one only of these effects for each theory. On this theoretical basis, the combination of the two theories into a single, simple equation, which can still be used with ease at the applied level, leads to much better precision of forecasting of the gel point than any of the two theories from which the equation is derived and than any of the more complex theories in this field. © 1996 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 603–617, 1997

Key words: polymer networks, polycondensation, gel point, degrees of freedom, gel theories, networking, glass transition temperature, thermomechanical analysis, molecular mechanics

INTRODUCTION

Theories and methods defining and modeling the formation of polymer networks already exist.^{1–3} The most useful of such theories, most useful purely from an applied everyday use, are often the

simpler and older ones.^{4–7} More complex theories, although often excellent at describing to a much greater and thorough extent the molecular reality of gelation suffer also of the defect of being rather difficult to use and unyielding for everyday practice and thus remain rather unapproachable to those who could benefit most from their application for the easy resolution of applied problems.

Many of such theories concentrate on the deter-

mination, by different mathematical approaches and different physicochemical approximations, of the degree of conversion, and, hence, of the advancement of polymerization at the point of gel and on the calculation of basic polymer parameters derived from the determination of the gel point. Among these in the field of polycondensation, the following must be remembered: (1) the gel theory of Carrothers,⁴ in which the critical degree of conversion at the gel point (p_{gel}) is defined as $p_{\text{gel}} = 2/f$, with f being the average functionality of the monomers in the system; (2) the probabilistic gel theories of Flory⁵⁻⁷–Stockmayer,^{8,9} in which p_{gel} is defined through the coefficient of branching $\alpha = 1/(f - 1)$, f being the functionality of the monomer of greater functionality, through the expression $\alpha = rp^2\rho/[1 - rp^2(1 - \rho)]$, where p is both the degree of conversion and the probability that a certain reactive group has, in fact, reacted, ρ is the proportion of such reactive group belonging to branching units, and r is the ratio of the number of reactive groups of the two monomers participating to the polycondensation; (3) the cascade process theory of Gordon,^{10,11} based on more complex functions than the two preceding ones but also offering some further advantages over them; (4) the Miller–Macosko¹² recursive method; and (5) the stochastic graphs theory of Bruneau,^{13,14} which is more complete but very complex and very complicated to use; in addition to even more complex theories which can be found in the review literature.^{2,3} Among these, the first two are of such a simplicity to be constantly used in applied practice, and the third and fourth one are also sometimes used. They all suffer from some defect; the Carrothers theory, for instance, overestimates the numerical value of p_{gel} , while Flory's theory underestimates it, but they are nonetheless extremely useful to solve applied problems. Furthermore, they do not describe what happens in the system between the reaching of the gel point and complete hardening of the network.

Recently, work on the formation of polymer networks by photopolymerizable and polyester surface finishes on wood has yielded a mathematical relationship^{15,16} between the energy of interaction (E) at the finish/wood interface calculated by molecular mechanics (work of adhesion); the number of degrees of freedom (m) of the segment of the synthetic polymer between two cross-linking nodes; the coefficient of branching α , hence, the functionality of the starting monomer; and the relative deflection (f) obtained by thermomechanical analysis (TMA) of wood specimens

coated with the photopolymerizable finish through the expression $f = km/\alpha E$, where k is a constant.^{15,16} Indications were also obtained that such a relationship is also valid for polycondensation resins.¹⁶ In this paper, such a relationship is used first to show that correlation between these different parameters indeed exists also for polycondensation resins and, secondly, that regression equations correlating directly m with E and m with f can be derived for hardened phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), melamine-formaldehyde (MF), and tannin-formaldehyde (TF) resins. These relationships will then be used to correlate the number-average degree of polymerization (DP_n) and p_{gel} with m , leading to simple and easily applicable extensions of the combination of the two theories of Carrothers and Flory. It must be clearly pointed out that this work does not describe a new gel theory but simply an applicable refinement of the combination of two existing ones, leading to better correlation with experimental results while maintaining ease of application. It must be equally pointed out, however, that an alternate approach to glean information on physicochemical characteristics of the networking process and of networked, hardened polycondensates is also presented.

EXPERIMENTAL

Resins Used

The resins used were as follows.

1. An industrial pure resorcinol-formaldehyde cold set resin of solids content of 53%, of pH 8.3, of manufacturing molar ratio R : F = 1 : 1.5, to which was added 1 further molar proportion of paraformaldehyde as hardener to yield a final molar ratio of R : F = 1 : 2.5, supplied by Bakelite AG (Duisburg-Meiderich), Germany, and specifically prepared for these series of experiments.
2. An industrial MF thermosetting resin of molar ratio M : F = 1 : 1.5, of whitening point = 130%, of pH 10.2 and of solids content of 63%, prepared by Chimica Pomponesco, Italy, to which was added 1.5% NH_4Cl as hardener.
3. A PF thermosetting resol resin of molar ratio 1 : 2.0, of solids content of 51%, of pH

Table I Experimental Deflection, Energy, and Degrees of Freedom Results Leading to Regression Eqs. (2), (3), and (4) for Melamine-Formaldehyde-(MF), Resorcinol-Formaldehyde-(RF), Phenol-Formaldehyde-(PF), and Quebracho Tannin-Formaldehyde (QF)-Hardened Polycondensation Networks and Results Derived for Other Resins

Resin Type	f	α	αf	E (kcal/mole)	m
	(μm) experimental				
MF	15.0	0.2	3.0	10.3 ^a	1.9
RF	13.5	0.5	6.75	14.5 ^a	6.1
PF	20.1	0.5	10.05	14.5 ^a	9.1
QF	24.1	0.5	12.05	13.59 ^a	10.2
QF	24.1	0.148	3.58	12.12 ^a	2.7
TMPTA	63	0.2	12.6	13.58 ^a	11.0 ^b
TPGDA	49	0.33	16.2	13.83 ^a	14.3 ^c
Polyester	28	0.33	9.2	13.70 ^a	7.9 ^d
PineTF dimer	32.3	0.5	18.09	14.17	16.05
PineTF real	32.3	0.168	5.43	13.00	4.4
PecanTF dimer	28.9	0.5	14.5	14.07	12.7
PecanTF real	28.9	0.182	5.26	13.26	4.3
PVAc (35°C)	31.2	1	31.2	—	28.1
PVAc (60°C)	50.0	1	50.0	—	45.4
PVAc (80°C)	57.3	1	57.3	—	52.7
PVAc (100°C)	62.5	1	62.5	—	56.9
PVAc (120°C)	65.6	1	65.6	—	59.7

^a Energy results determined by molecular mechanics.^{15–21}

^b Experimental result: 11.0.

^c Experimental result: 14.0.

^d Experimental result: 8.0.

that, for instance, there is a small proportion of slightly longer segments in between the nodes; in reality, the likely length distribution is likely to be more complex with different proportions of 0, 1, 2, 3, and 4 or more resorcinols for each single segment between network nodes, yielding an average of $m = 6.12$. Figure 1 shows the regression line passing through the five cases, namely, RF, MF, PF, and QF dimers, for which f , α , and E are known.^{17–21} These five cases lead to the following regression equations.

$$m = 0.919\alpha f - 0.579 \quad (2)$$

$$E = km / (0.1081m + 0.683) \quad (3)$$

$$E = k / (0.919 - 0.579 / \alpha f) \quad (4)$$

All equations have the coefficient of correlation $r = 0.996$.

These regression equations have perhaps a better applied use than the generalized formula because they express any of the two more difficult or time

consuming parameters to obtain, namely, m and E , as a function of only one of the other parameters.

The second section of Table I presents the characteristic values of f , α , m , and E of three radical addition polymer networks on wood, the only three other polymers for which all such values are known and have been obtained independently, namely, the networks obtained from trimethylolpropane triacrylate (TMPTA), tripropyleneglycol diacrylate, and a maleic/ethylene glycol polyester resin,^{15,16} calculated through regression eq. (2). It can be seen that all these three cases also fall well on the regression line in Figure 1, indicating that both the original formula, as well as the three regression equations reported above, not only show good correspondence with the experimental results but also have wider applicability than just to polycondensates, at least being valid also for hardened networks formed by radical addition polymerization. The third section in Table I instead shows the results of m and E forecasted through the use of the same regression equations for the two cases each of pine tannin/formaldehyde and Pecan tannin/formaldehyde

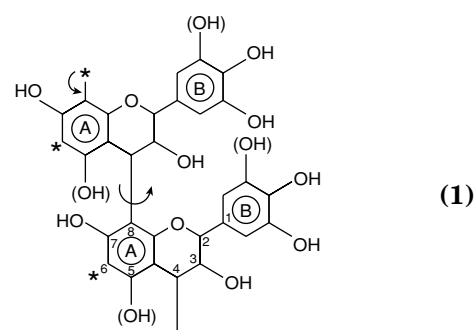
Table II Variation as a Function of Temperature of TMA Measured Deflection and Number of Degrees of Freedom m Calculated Through Eq. (2) for the Gelling and Subsequent Hardening of Different Polycondensates (f in μm)

Temperature (°C)	TMA Bending (μm)									
	RF		MF		PF		QF		PineTF	PecanTF
	f	m	f	m	f	m	f	m	f	f
30	61	27.5	103.1	18.4	71	32.0	102.1	13.3	91	188.4
40	67	30.2	104.6	18.6	68	30.7	103.7	13.6	88	145.5
50	73	33.0	112.3	20.1	64	28.8	—	—	90	127.8
60	76	34.3	116.9	20.9	59	26.5	106.7	14.0	90	107.8
70	91	41.2	122.5	21.9	59	26.5	106.7	14.0	84	75.6
80	79	35.7	125.5	22.5	56	25.2	106.7	14.0	67	52.2
85	66	29.7	—	—	—	—	—	—	—	—
90	51	22.9	126.2	22.6	50	22.4	89.9	11.7	57	38.9
95	37	16.4	—	—	—	—	—	—	—	—
100	30	13.2	115.4	20.6	45	20.1	80.8	10.4	50	30.0
110	19.4	8.3	88.6	15.7	40	17.8	53.4	6.7	42	28.9
115	—	—	81.5	14.4	—	—	—	—	—	28.9
120	19.4	8.3	61.5	10.7	39	17.3	48.8	6.1	34	28.9
125	—	—	47.7	8.2	—	—	—	—	—	28.9
130	18.7	8.0	30.2	5.0	30	13.2	32.0	3.8	31	—
135	—	—	21.5	3.4	—	—	—	—	—	—
140	18.0	7.7	13.8	2.0	20.2	8.7	24.4	2.7	31	—
150	18.0	7.7	10.8	1.4	18.2	7.8	24.4	2.7	30.1	—
160	18.0	7.7	10.8	1.4	18.2	7.8	24.4	2.7	30.1	—
170	18.0	7.7	10.8	1.4	18.2	7.8	24.4	2.7	30.1	—

polycondensation-hardened networks. For the three tannin-formaldehyde cases, quebracho, pine, and pecan, the results were first calculated for dimers and afterwards for the real number-average degree of polymerization obtained experimentally for these tannins^{22,23}; all cases again fall on the same regression line (Fig. 1).

It is interesting to compare the relative results of the polycondensates in regard to the density of cross-linking (the lower is the value of m , the higher is the density of cross-linking of the hardened network). From the results in Table I, it can be noticed that the highest density of cross-linking is for a MF resin, aminoplastic resins being known to have high cross-linking density,²⁴ followed by the RF resins, and then only by the thermosetting PF resin, this order being supported by dry strength results^{24,25} and qualitative cross-link densities per unit volume reported for these resins. More interesting is the case of the three tannins in which for the higher oligomers reacted with formaldehyde, quebracho tannin has a higher cross-linking density than the other two tannins (which, instead, present little difference between each other), while the dimers have a similar but more differentiated

trend. It is necessary to discuss more in depth the case of the tannins, as the numerical values obtained for m have a somewhat different meaning than for the synthetic resins. While in all the synthetic resins, the degrees of freedom of the network segments are the two rotatable bonds, each surrounding a methylene bridge $-\text{CH}_2-$, this is not the case in the tannins. Thus, a tannin dimer already presents an internal skeletal degree of freedom between the two flavonoid units before the appearance of any methylene bridges.



* = sites reactive with formaldehyde

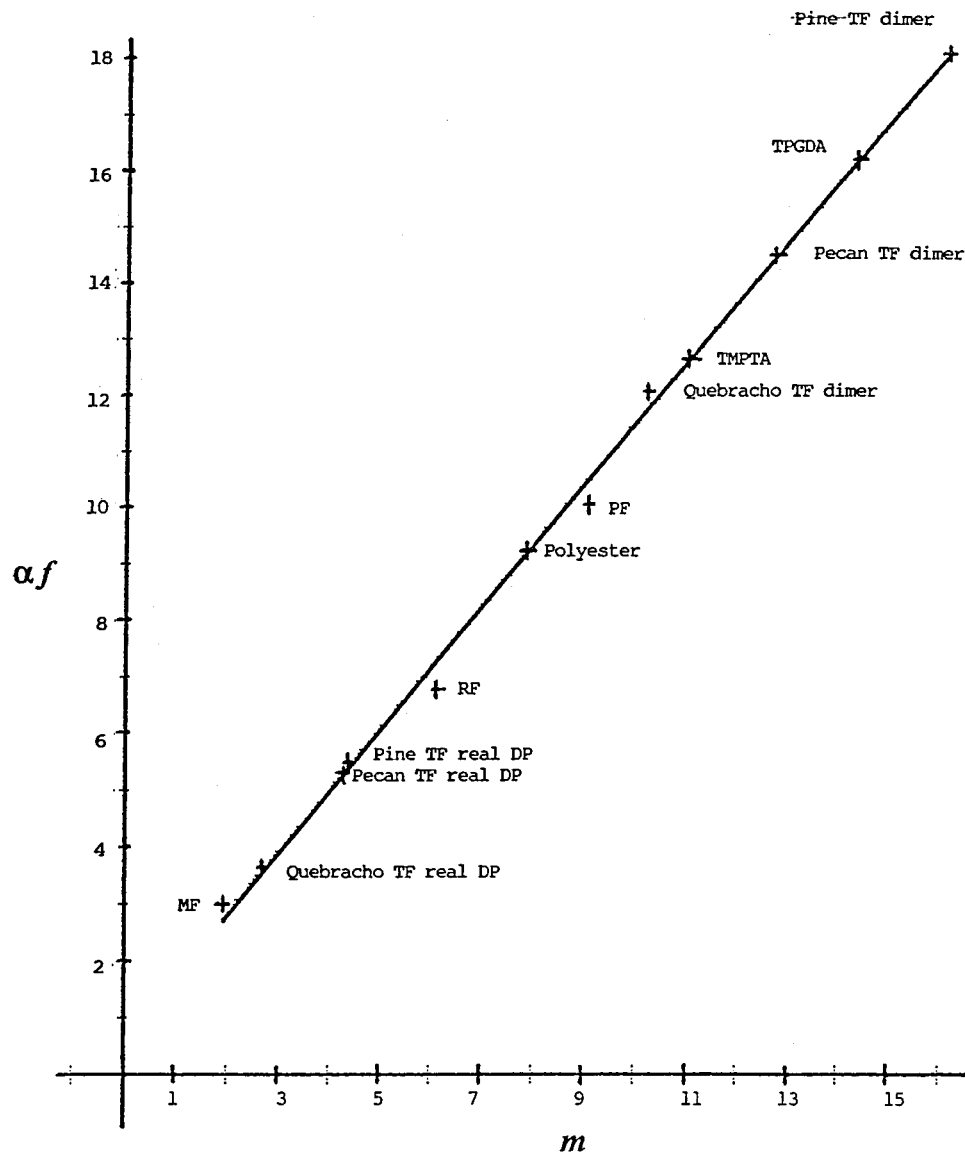
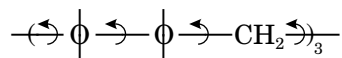


Figure 1 Graphic representation of regression eq. (2) and the position of the experimentally obtained points for different completely hardened polycondensation networks from which the equation is derived.

This must also be kept into account. Thus, for a quebracho dimer, the value of $m \sim 10$ means



$$m = (1/2 + 1 + 1 + 1/2) \times 3 = 9$$

Thus, there are six flavonoid monomer units between the two nodes for a total of nine degrees of freedom, plus $2 \times \frac{1}{2} =$ one additional degree of freedom from the $-\text{CH}_2-$ part of the two bridges attached to the cross-link nodes, for a total of ten degrees of freedom. In the case in which the experi-

mental number-average degree of polymerization of quebracho tannin is used, the numerical value of m obtained is of 2.7. This means that the internal and $-\text{CH}_2-$ condensation-derived degrees of freedom are equivalent and cumulative. The real situation is, of course, that of the higher oligomer, not of the dimer, and the resorcinol nature of the flavonoid tannins places them quite logically not far from pure resorcinol resins on the scale of density of cross-linking depicted in Figure 1. Applied experimental evidence supports this as tannins are the only materials used today to substitute resorcinol in RF and PRF adhesives.²⁶⁻²⁹

The results and correlations presented lead to

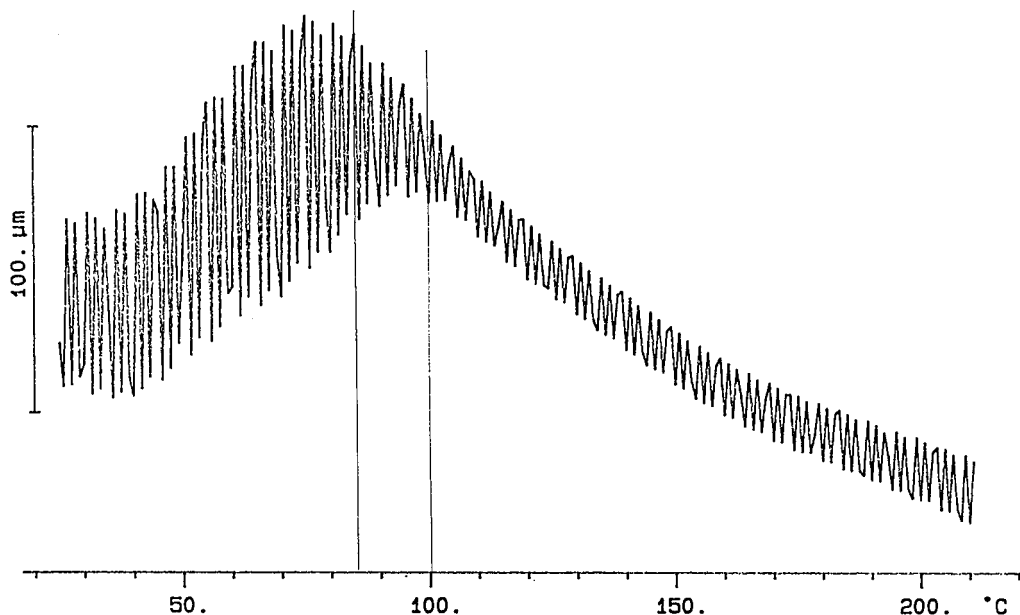


Figure 2 Example of one dynamic TMA curve obtained during gelling and hardening of a resorcinol-formaldehyde (RF) polycondensate while increasing temperature at 10°C/min. Note the short range variation in amplitude of the deflection with increasing temperature, which is used for the calculations in the text. The overall trend of the curve pertains to standard considerations in TMA and does not concern the calculations in the text.

the conclusion that it is possible to follow through the variation of the value of m and, in a quantitative manner, the progress of networking after the gel point of a polycondensation. To this effect in Figure 2, it is shown the TMA trace in flexion for the RF wood joint. In Figure 3, the variation obtained for RF resins from 30° to 140°C in relation to the regression line of αf as a function of m is shown. At 30°C, while the resin is still liquid and far from the gel point, thus, where m between cross-linking nodes definitely has no meaning, the point having coordinates $(\alpha f, m)_{30^\circ\text{C}}$ falls well out of the regression line. As the temperature increases, already at 40°C, the point $(\alpha f, m)_{40^\circ\text{C}}$ still falls outside the regression line, but it is already much nearer to it, already at 50°C and higher temperatures, the points all fall on the regression line. Two competing effects are noticeable, namely, the increasing temperature, increasing chain mobility, and lowering viscosity, as well as the increasing size of the polymer due to the acceleration of the polycondensation, which also is the consequence of the increasing temperature. It is possible to see that initially the molecular mobility and viscosity reduction effect predominates; hence, the value of m increases up to a temperature of 70°C. After 70°C, the polymerization becomes the predominant effect, and, as a conse-

quence, molecular mobility decreases both before and after the gel point to give decreasing values of m . There are several features of interest in Figure 3. First of all, all points of coordinates $(\alpha f, m)$ are located on the regression line, except for the initial 30°C one and 40°C (much less out) one. Polymerization has then definitely started to predominate by 70°C, and all the points clearly indicate that m decreases as first the polymerization and then the hardening proceed. This behavior appears to be the same for all the polycondensates investigated (Table I); the only parameter that changes is the temperature at which the inversion of movement from towards higher m to towards lower m occurs, which is different for the different polycondensates.

If, for instance, a RF resin of initial molar ratio R : F = 1 : 2.5 is considered, its gel point according to Flory's theory is reached when $p_A = (\frac{3}{5})p_B$; thus, from $\alpha = rp^2$ for a max functionality of 3 (resorcinol), $p_B^2 = (\frac{3}{5})0.5$, and $p = 0.913$; as a consequence, $DP_n = 1/(1 - p) = 11.49$. As $[-\phi-\text{CH}_2-]_n$ presents $2n = m$ degrees of freedom, it means that $m = 2DP_n$; thus the p_{gel} of 0.913 is achieved at $m = 22.99$. From the experimental data in Table II and from Figure 2, it means that the gel point of the system intervenes at 91°C. Furthermore, since $m = 2DP_n$ and DP_n

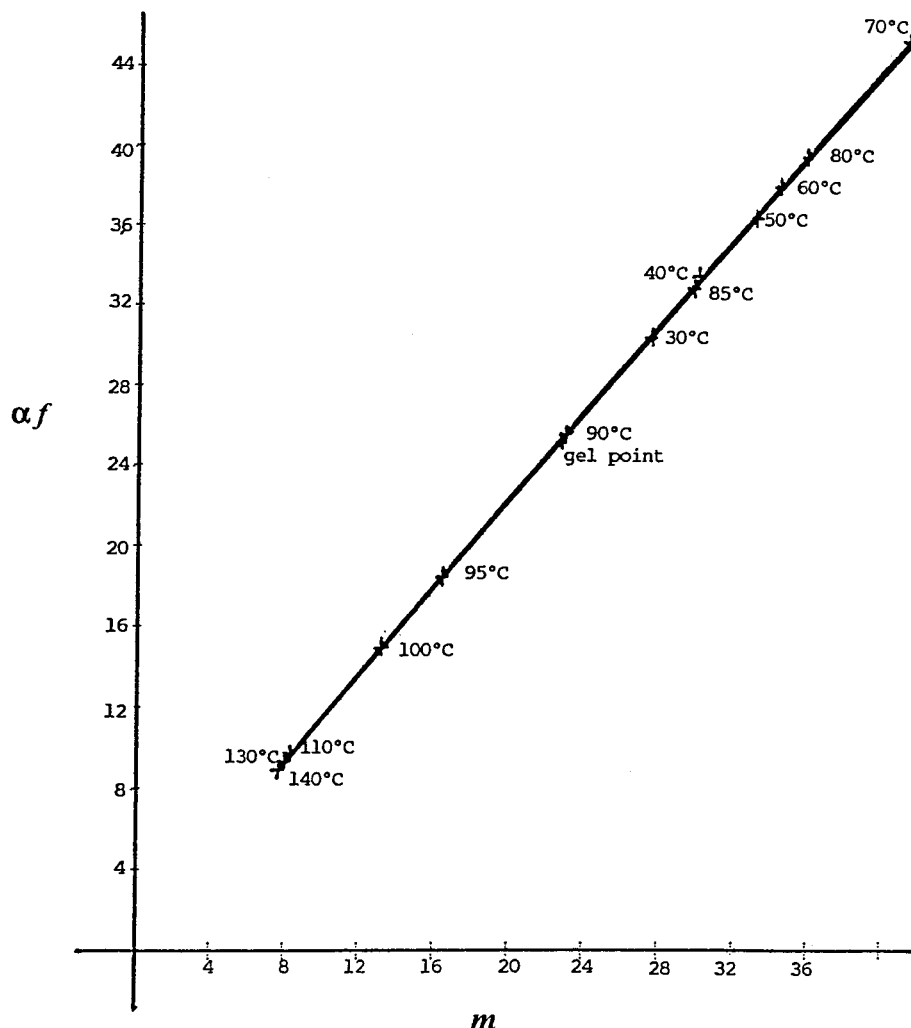


Figure 3 Example of graphic representation of the relative movement on the regression line derived from eqs. (1) and (2) of the experimental points pertaining to the gelling and hardening of a polycondensate, the resorcinol-formaldehyde (RF) resin of Table II.

$= 1/(1 - p)$, then $m = 2/(1 - p)$; hence, there is a relationship between the degree of conversion p and m . That this is valid from $p = 0$ and $m = 2$ (no polymerization) to $p = 1$ (complete conversion) is just nothing other than expressing the Carothers equation in m rather than DP_n , but as at $p = 1$, $m = \infty$, thus a molecule infinitely long, this means that after the gel point p can become greater than 1 in order to be able to describe the process of hardening. This is a logical conclusion as, for instance, if for a polycondensation between a trifunctional and a difunctional monomer, the gel point intervenes at complete conversion, hence at $p = 1$, then also $p_{\text{gel}} = 1$. This means that after the gel point, the reaction continues to form a tridimensional network and after the gel point $1 < p < 2$ and $\infty > |m| > 2$, the formula above can

then be written just as $m = 2/(1 - p)$ with m yielding a negative value only after the gel point to indicate that it is in the domain between gel and complete hardening, or otherwise $m = \text{absolute value of } 2/(1 - p)$. As the gel point rarely intervenes at $p = 1$ and as the relative proportions of the two reactive groups taking part in the polycondensation is important to define p , p_{gel} , and m , the expression can be modified to take into account the relative proportions of reactive groups. According to Carothers, $DP_n = 2/(2 - fp)$, then $m/2 = 2/(2 - fp)$; thus, finally

$$m = 4/(2 - fp) \quad (5)$$

and, vice versa, $p = (2m - 4)/fm = 2/f(1 - 2/m)$ where f is Carothers' average functionality of the

Table III Number of Degrees of Freedom, Degree of Conversion, Number-average Degree of Polymerization, and Temperature at Gel Point for Different Polycondensates Obtained From the Experimental Data in Table II

Resin Type	m_{gel}	p_{gel}	$DP_{n\text{gel}}$	T_{gel} (K)
RF 1 : 2.5	23.0	0.913	11.5	363
MF 1 : 1.5	5.4	0.633	7.0	402
PF 1 : 2.0	10.9	0.817	5.5	408
PF 1 : 2.2	13.9	0.856	7.0	400
QF real	9.7	0.794	4.9	375
QF dimer	21.7	0.908	10.8	393

whole polycondensation system. It must be clearly pointed out that such an equation functions exclusively for the Carrothers-defined value of average degree of functionality f and thus for the Carrothers defined $p_{\text{gel}} = 2/f$ value. If the p_{gel} is calculated by Flory's method, which takes into account the functionality already in the calculation of p_{gel} , then eq. (5) is not valid, but the more general eq. (6) is valid for both theories

$$m = 2/(1 - p) \quad (6)$$

and, vice versa, $p = (m - 2)/m$.

Equation (5) then indicates that, in theory, at the exact instantaneous gel point, m is infinite; thus a linear polymer infinitely long with no cross-links. As the system proceeds over the gel point, then cross-linking has started, and m starts to describe the average number of degrees of freedom of the average length segment between cross-linking nodes from the initial to the final tridimensional network. Thus, in eq. (5) before and up to the gel point, $0 < p < p_{\text{gel}}$ and $2 < m < \infty$, and after the gel point to complete hardening, $p_{\text{gel}} < p < 2$ and $\infty < |m| < 2$.

These equations, as well as the $DP_n = 1/(1 - p)$ equation are valid both before and after the gel point of the system, thus from the polycondensation beginning through to its gel point and further onto its formation of the complete, final hardened network. From these expressions, the values of p , DP_n , gel temperature (t_{gel}°), and p_{gel} can be obtained with ease by a simple TMA measure of deflection and the calculation of m according to regression eq. (2), $m = 0.919\alpha f - 0.579$. Thus, to check this, in Table III, the values of m_{gel} , $DP_{n\text{gel}}$, gel temperature (T_{gel}), and p_{gel} are obtained from the values of p_{gel} obtained according to Flory's theory (see the example of RF resin, above), which gives DP_n and m through eq. (6), and T_{gel} is derived from the values of m shown in

Table II. The expressions have been found to be valid for all the polycondensation resins tested (Table I), but it must be kept in mind that as α in eq. (2) is Flory's α , if such a regression equation is to be used, then it must be expression (6).

Again, from Flory's $\alpha = rp_{\text{gel}}^2$ and from $f = km/\alpha E$ expressing the latter in α , it is obtained that $\alpha = km/fE$ and, as a consequence, $km/fE = rp_{\text{gel}}^2$, which indicates that not only m and p are related throughout the whole range of polymerization and hardening and that in Flory's theory, m_{gel} is never infinite (Table III), as expected, but that p and E are inversely proportional. The higher the value of p , the lower is the the value of E , and vice versa, confirming an already known adhesion effect of polycondensates at the polycondensate/substrate interface.¹⁷⁻²¹

An interesting point emerging from Table II is that, in general, while well before gel point during the initial stages of the reaction, $m \sim T$ (absolute temperature); later, hence before and after gel point, $m \sim 1/T$. Thus, before the gel point, just in the initial stages of the reactions, from the expression relating apparent molecular weight between entanglement couplings and the rubber plateau modulus (G_N°) in the theory of rubber elasticity^{30,31} $G_N^\circ \sim (\rho/M_e)RT$, where ρ is the density, M_e is the apparent average molecular weight between entanglements, R is the gas constant, and T is the absolute temperature. Resolving in M_e , then $M_e \sim (\rho/G_N^\circ)RT$, where M_e is a function of m because as $M = M_0DP_n$, where M_0 is the molecular weight of the repeating unit of the polymer, then $M_e = M_0DP_{ne}$; but from $DP_n = m/2$, then $M_e = (m_e/2)M_0$. Thus

$$m_e \sim (2\rho/M_0G_N^\circ)RT \quad (7)$$

where m_e is the number of degrees of freedom of the chain segments between entanglement cou-

plings, this equation explains the direct dependence of the average m of the system from the temperature. As a consequence, in the initial stages of the reaction, well below the gel point, the systems are clearly only composed of entangled molecules and not of cross-linked ones. The fact that the relation between m and the temperature changes already well before the gel point indicates that branching of the molecule, hence, the formation of sites of incipient cross-linking, generally starts well before the gel point.

All the above means also that in noncross-linked networks, such as $m \sim T$, then also $2/(1-p) \sim T$ and, thus, $p \sim 1/T$. Translating this to a polycondensation reaction well before the gel point, it means that if one disregards the important effect of the proceeding polymerization (for which kinetic control clearly indicates that as T increases, p increases too); thus, if one takes the case of a polycondensation well before gel point when the polymer chains are still substantially linear, then the value of p at which branching starts should be lower the higher is the temperature.

After the gel point, always $m \sim 1/T$ as T increases when $|m|$ decreases (the network proceeds to greater density of cross-linking). The relationship between m and T is not, however, a linear one. From Table II, using, for instance, the RF's case and using the inverse of the absolute temperature $1/T$, the regression between the two parameters yields

$$|m| = 0.00352e^{3097.7(1/T)} \text{ or equally} \\ \ln |m| = 49.7 + 7.95(1/T) \quad (8)$$

with coefficient of correlation $r = 0.90$. The above and the dependence of m from the temperature confirms that the expression $f = km/\alpha E$ appears to be valid for both covalently bonded networks as well as for entangled, noncovalently bonded networks. Thus, before reaching the gel point and before branching, a polycondensate will show that the higher is $T =$ greater molecular movement $=$ greater $M_e =$ greater value of m . After starting to branch and particularly after the gel point two trends are present, namely, (1) higher $T =$ greater molecular movement $=$ greater $M =$ greater m , and (2) higher $T =$ further progress of the reaction ($p > 1$) $=$ smaller $M =$ smaller m .

After branching and after gel point, the second effect clearly predominates. The first effect is less significant simply because the formation of the network and introduction of the cross-linking

nodes constrains the molecular mobility of the system.

The type of dependence from the temperature reported above indicates that in polycondensate-hardened networks, thus after the gel point of the reaction, $m \sim 1/T$. From eqs. (5) and (6), $m = 4/(2 - fp)$, which means that $p \sim T$; which means that after the gel point, in the network, as the temperature increases, as expected, $|m|$ decreases (Table II), and p increases, demonstrating again that reaction continues after the gel point and also well after the network has already formed. In this regard, it is of interest that comparing the Dibenedetto equation³² and the Couchman equation,³³ an equation³⁴ is obtained correlating the ratio of the mobilities of the segments between cross-linking nodes, covalent or not, for a polymer having a degree of conversion p with the apparent rate constant of the reaction. This expression is

$$\lambda p/[1 - (1 - \lambda)p] = 1 - e^{-kt} \quad (9)$$

where λ is the ratio of the mobilities of the segments for a degree of conversion, k is the apparent rate constant of the curing reaction, and t is the time in seconds. However, the mobilities of the segments in between nodes of a polycondensation network are nothing other than the starting and end values of $|m|$, the number of degrees of freedom of the same segments which can be obtained through eqs. (1) and (2). Thus, the above equation can be written as

$$[(m_{\text{end}}/m_{\text{start}})p]/[1 - (1 - (m_{\text{end}}/m_{\text{start}}))p] \\ = 1 - e^{-kt} \quad (10)$$

where $\lambda = (m_{\text{end}}/m_{\text{start}})$. Taking this equation, it is possible to calculate the rate of hardening of a polycondensation network at any predetermined temperature. The TMA experiment should be isothermal. Trying this relationship with an RF resin of the same type used for all the other experiments at a constant 115°C temperature and taking as starting point the gel point at which $m_{\text{start}} = 23$ and $m_{\text{end}} = 7.7$, the transformation taking 300 s yields a value of $k = 5 \times 10^{-3} \text{ s}^{-1}$. In this context, applying such equations to the values in Table II, thus in nonisothermal conditions, it can be deduced that the type of dependance from the temperature of the hardening of the network is consistent with more recent views³⁵⁻³⁸ that two molecular phenomenons occur during thermosetting polymers curing. The first is gelation, which

corresponds to incipient formation of an infinite network; the second is vitrification, which occurs when the glass transition temperature (T_g) of the reacting mixture rises to the cure temperature. At gelation, resin fluidity decreases substantially. However, conversion is far from complete, and the reaction rate is kinetically controlled. With continuing cure, the T_g reaches the curing temperature, and vitrification occurs. At that point the reaction rate becomes diffusion controlled and is drastically reduced. However, what has been advanced, which the equations above (as well as the results in Table II) appear to disprove is that if the temperature is later raised above the initial cure temperature, the material softens, and the cure rate accelerates again until T_g increases to that new temperature. From the results in Table II and the eqs. (9)–(11), this is clearly not the case. Such a behavior might well occur if reactive sites and reactive groups are still available; but on exhaustion of the reactive sites and groups,³⁹ or on reaching the ultimate network in which degrees of freedom are very low, this behavior clearly cannot occur. As the equation of Dibeneditto³² relates the variation of the glass transition temperature T_g as a function of the right-hand term of eqs. (9) and (10), the above also means that T_g can be measured through the value of m obtained by molecular mechanics calculations and, vice versa, that m can be calculated from the value of T_g obtained experimentally, for instance from differential scanning calorimetry, through the expression

$$\begin{aligned} [(m_{\text{end}}/m_{\text{start}})p]/[1 - (1 - (m_{\text{end}}/m_{\text{start}}))p] \\ = (T_g - T_{g0})/(T_{g,\text{infin}} - T_{g0}) \quad (11) \end{aligned}$$

or equally

$$\begin{aligned} [(m_{\text{end}}/m_{\text{start}})(m - 2)/m]/ \\ [1 - (1 - (m_{\text{end}}/m_{\text{start}}))(m - 2)/m] \\ = (T_g - T_{g0})/(T_{g,\text{infin}} - T_{g0}) \quad (11a) \end{aligned}$$

where p can be expressed as a function of m by substituting in (11) eq. (6), namely, $p = (m - 2)/m$, to yield a direct relationship between the number of degrees of freedom and the glass transition temperature. T_{g0} is the glass transition temperature of the reactive blend at time = 0; thus at a zero degree of conversion, $T_{g,\text{infin}}$ is the glass transition temperature for a completely cured polymer hence extrapolated to maximum theoretical degree of conversion, and T_g is the

glass transition temperature corresponding to the degree of conversion p . It must be pointed out that eqs. (9), (10), and (11) can be used in the case of $0 < p < 1$.

All the above indicates that both in Carrothers' and in Flory's theory, even eliminating the kinetic control of the reaction and just under thermodynamically or diffusion controlled conditions, the p_{gel} depends to a certain extent on the temperature. The consequence of this is that the theories of both Carrothers and Flory, respectively, might overestimate and underestimate the value of p_{gel} also for not taking this factor into account. While Stockmayer⁸ has demonstrated that Flory's theory is in good agreement with experimental results, if formation of cycles is eliminated, the theory as it stands underestimates p_{gel} because it does not cover the case of the cycles formed during reaction. This cannot be said for Carrothers' theory, which overestimates the gel point. It means that Carrothers' formulas are capable of taking into account the formation of cycles, but they continue overestimating the gel point as a consequence of another factor, which is likely to be the temperature effect described above. This means that a theory, Flory's, does miss only one effect (cyclization), but, in principle, not the other (as based on molecular motions dependence from the temperature, a probabilistic theory also implies dependence of its calculated p_{gel} from the temperature); and a theory, Carrother's, does take into account cyclization but misses the temperature effect (before gel point, what is said above, namely, that for the small thermodynamic control component, $p \sim 1/T$, means that as the temperature increases and the system proceeds towards branching the value of p_{gel} decreases; if the effect is not considered, then the calculated value of p_{gel} will be higher; thus, it will overestimate the experimental value of p_{gel}).

The above leads to the conclusion that if an exact value of p_{gel} is needed, then probabilistic expressions for cyclization reactions need to be introduced in Flory's formula, and this would be rather difficult and lead to a very complex and impractical formula to use; otherwise, the thermodynamic dependence from the temperature needs to be introduced in Carrother's equation, also leading to a more complicated formula to use. Thus, both the two conceptually correct approaches just outlined do not satisfy the need for a simple formula, which can be used in practice and is capable of forecasting with enhanced precision the value of p_{gel} . Any of these routes leads ultimately to the type of more complex, difficult-

Table IV Comparison of Experimental Degree of Conversion at Gel Point with Values Forecasted by Different Theories and the Values Obtained Through Eq. (12)

Polycondensation System	p_{gel} (Experimental)	p_{gel} (Carrothers)	p_{gel} (Flory)	p_{gel} (Stochastic Graphs)	p_{gel} (Flory + Carrothers) ^a	p_{gel} (Weighted; Flory + Carrothers)
Glycerol ($f_A = 3$) + +Phthalic acid or phthalic anhydride	0.786 ^b to 0.796	0.833	0.707	0.800	0.770	0.782
+Succinic acid or succinic anhydride	0.760 ^b	0.833	0.707	0.800	0.770	0.782
+Adipic acid	0.755 ^b	0.833	0.707	0.800	0.770	0.782
+Sebacic acid	0.770 ^b	0.833	0.707	0.800	0.770	0.782
Pentaerythritol ($f_A = 4$) + adipic acid	0.606 ^b 0.63 ^c 0.65 ^d 0.623 ^e	0.750	0.577	0.666	0.663	0.681

^a See eq. 12.^b See Kienle and Petke.⁴⁰⁻⁴²^c See Stockmayer and Weil.⁸^d See Walker and Mackay.⁴³^e See Gordon and Scantlebury.⁴⁴

to-use theories discussed in the introduction. However, another conceptually correct but much simpler approach can be taken; but for this, a conceptual approximation needs to be made, namely if the extent of variation from reality of one theory due to disregarding the thermodynamic contribution to temperature is considered approximately equivalent to the extent of variation from reality of the other theory due to the disregard of the concomitant cyclization reactions; as the two factors disregarded pull the value of p_{gel} in different directions than a rather simple formula, averaging the forecasts of the two theories might well enhance to some extent the precision of the forecast. Thus, from Flory's $\alpha = rp_{\text{gel}}^2$ and from Carrother's $p_{\text{gel}} = 2/f$, a formula of type

$$p_{\text{gel}} = (2/f + V\sqrt{\alpha/r})/2 \text{ or}$$

$$p_{\text{gel}} = 1/f + (\frac{1}{2})V\sqrt{\alpha/r} \quad (12)$$

can be proposed. * To control that this formula can forecast with enhanced precision the value of p_{gel} , it is necessary to compare its results with both experimental results and with the results of other theories. In Table IV are shown the experimental values⁴⁰⁻⁴⁴ of p_{gel} and forecasted according to the

*In the absence of difunctional monomers substitute α/r for $\sqrt{\alpha/r}$ in eq. (12).

Carrothers', Flory's, and the much more complex stochastic graphs theories, compared with the results of eq. (12). The simple eq. (12) yields, in all cases, results that are closer to the experimental values than all the others. If the discrepancies in the values of the average functionality f of the system between the experimental values of p_{gel} and calculated p_{gel} are back-calculated from these, it is possible to see that the difference between p_{gel} for experimental, Carrothers', and eq. (12) can sometime be narrowed further by giving a different weight to the two terms of eq. (12), hence, to the two theories contribution. The explanation of the possible improvement in results sometimes achievable by assigning a different weight to the two terms in eq. (12) is that the contribution of cyclization reactions varies by a certain extent under different reaction conditions. In Table IV (last column), an example of the results obtained by weighing differently the two terms according to $p_{\text{gel}} = \frac{3}{5}f + (\frac{1}{5})V\sqrt{\alpha/r}$ is also shown. Equation (12) still gives a better result in the majority of cases. As the contribution of cyclization reactions is variable, as can be deduced by the variability of the experimental in relation to the calculated values of f in the cases in Table IV, then, as a consequence, just the use of different weights for the two different terms does not overcome the inherent variability introduced in the system. Expressions to describe cyclization reactions do exist³;

thus, backbiting cyclizations show a relation between the concentration ($[C_{CY}]$) of cyclic molecules and the concentration ($[C_{LI}]$) of linear molecules of $[C_{CY}] \sim kDP_n^{-1/2}[C_{LI}]$, while end-to-end cyclization shows a relation in which $[C_{CY}] \sim kDP_n^{-3/2}[C_{LI}]$. This means that at equal $[C_{LI}]$ and DP_n , the former contributes $DP_n^{-1/2}$ and the latter $DP_n^{-3/2}$ to the total number-average degree of polymerization of the system. In polycondensation in general, only the former type of cyclizations occur.³ For example, at the DP_n of 3.41, hence, $DP_n = 1/(1 - p)$ for a Flory's p_{gel} of 0.707 (Table IV), $p_{gel} = 1 - 1/(3.41 + 1.09) = 0.778$, an excellent fit. The problem is again that this is a general rule only, and as it is recognized that the extent of cyclization reactions varies,³ such a rule is just as conceptually limited as eq. (12), often giving slightly worse rather than slightly better results (Table IV). Thus, if preferred, rather than eq. (12), p_{gel} could be obtained by the following equation:

$$p_{gel} = 1 - 1/(DP_{nLI} + DP_{nCY}) \quad (13)$$

as soon as it is kept in mind that while acceptable solutions are obtained, these are still slightly worse than those obtained through eq. (12) and that, again, the inherent variability of cyclization reactions is not taken into account. This shows also that the error introduced into the Carrothers' equation for p_{gel} by the temperature effect already outlined above is of the order of between 44 and 50% of the error in such an equation, the rest being approximately accounted for by the cyclization reactions.

An interesting concept is to homogenize the two terms of eq. (12), hence to express both terms on the basis of the functionality of the two monomers, then eliminating the need to have to use Carrothers' average functionality of the system f in one term and the functionality and relative proportion of both reactive groups, which appear in the form of Flory's α and r in the second term. Thus, as Flory's $r = (f_A n_A)/(f_B n_B)$ and $\alpha = 1/(f_A - 1)$, where f_A and f_B are the functionalities of reactants A and B, respectively, with A being the monomer of higher functionality, and n_A and n_B their relative molar proportions, Carrothers' average functionality of the system can be defined as $f = (f_A n_A + f_B n_B)/(n_A + n_B)$, then substituting in eq. (12),

$$p_{gel} = (n_A + n_B)/(f_A n_A + f_B n_B) + \left(\frac{1}{2}\right) \sqrt{f_B n_B / [f_A n_A (f_A - 1)]} \quad (14)$$

It is easy to see from this expression that the first and second term present nonlinear relationships of different kinds between p_{gel} and each of the monomer functionalities, again indicating that on top of the basic phenomenon of gelling, they each describe different additional effects. It means also that α can be expressed in f , average functionality of the system; hence, the Carrothers' way and not only in f_A or f_B , and Carrothers' p_{gel} can equally be expressed in Flory's f_A and f_B rather than just f ; hence, for instance, $p_{gel} = (\sqrt{\alpha_{Carrothers}/r} + \sqrt{\alpha_{Flory}/r})/2$, where $\alpha_{Carrothers} = 1/(f - 1)$, and f is the average functionality of the system. In the first four cases in Table IV, such formula would give $p_{gel} = 0.776$, a very good value, but eq. (12) is still simpler and giving again a slightly more accurate result.

Equation (12) can be extended to any number of reactive monomers, not only two, and to the more complex cases in which every monomer can react with the others (but none with itself). In this case, the most general form of eqs. (12) and (13) is

$$p_{gel} = \sum n_X / \left(\sum n_X f_X \right) + \sqrt{\alpha / \left(\sum r_X + \sum r_X r_Y \right)} \quad (15)$$

which simplifies to eq. (14) for two monomers, which can only react with each other. In the case of three monomers in which one can react with the other two but where these last two cannot react with each other (i.e., resorcinol + formaldehyde + acetaldehyde), eq. (15) simplifies to

$$p_{gel} = \sum n_X / \left(\sum n_X f_X \right) + \sqrt{\alpha / \left(\sum r_X \right)} \quad (16)$$

A question that comes to mind, on seeing that on the graph in Figure 3, the points between 40 and 70°C, thus before network forming, also lie on the regression line, is if the general expression $f = km/\alpha E$ and, consequently, also regression eq. (2), are not only representative of polymer segments between nodes, which are due to covalent bonding, but also of linear polymers entanglement nodes, such as in linear thermoplastic polymers. To this purpose, polyvinyl acetate-bonded joints were also tested by TMA, both under constant and increasing temperature conditions (Table I), after being hardened at ambient temperature. The size

of the deflection obtained in bending, hence the number of degrees of freedom of segments between entanglement nodes, indeed increased with the increasing temperature,³² as it would indeed be expected. This, and other circumstantial evidence already presented is an indication that expression (1) might also apply to entanglement networks, but this cannot be concluded on the basis of the limited data available.

CONCLUSIONS

In conclusion, the use of eq. (1) yields a number of consequences of interest in the field of polycondensation-hardened networks and of their processes of hardening. From this equation, regression equations correlating only two parameters are obtained, which render easier the determination of the parameters that are more difficult or lengthy to obtain by experimental means. The process of networking, hence, of the reaction of polycondensation between the gel point and complete hardening of the network, can be followed by the determination of the average number of degrees of freedom m of the polymer segments between cross-linking nodes obtained through these equations. Even the equation of Carrothers can be adapted through the use of the average number of degrees of freedom of polymer segments between cross-linking nodes to describe the course of the polycondensation after the gel point and up to complete, stable networking. The dependence from the temperature of m can be connected to both the rate constant of advancement of the network and to the correlation of the value of m of the system to its glass transition temperature. Peculiarities in gel point forecasting by Flory's and Carrothers' theories, which depend on the well-known existence of reactions of cyclization during polycondensation, and by a thermodynamic temperature dependence not previously recognized, indicate that the gel point predicted by each theory fails to consider the existence of one and one only of these effects for each theory. On this theoretical basis, combination of the two theories into a single, simple equation, which can really be used with ease at the applied level, leads to much better precision of forecasting of the gel point than any of the two theories from which the equation is derived and than any of the more complex theories in this field.

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