

Rheology of Polyflavonoid Tannin–Formaldehyde Reactions Before and After Gelling. I. Methods

S. Garnier,^{1,2} A. Pizzi,^{1,2} O. C. Vorster,³ L. Halasz³

¹ENSTIB, University of Nancy 1, Epinal, France

²LERMAB, UMR 1093 INRA/UIHP/ENGREF, Nancy, France

³Technikon Pretoria, P.O.B. X 680, Pretoria, South Africa

Received 12 June 2001; accepted 14 December 2001

ABSTRACT: The gelling and hardening reactions of different, commercial polyflavonoid tannin extracts of the pro-robitenedin/profisetinidin, procyanidin, and prodelphinidin types with formaldehyde were studied by parallel-plate rheometry. To do this, methods to determine the rheological characteristics of tannin–formaldehyde polycondensation reactions both before and after the gel point were developed. The validity of some modifications of known methods was checked on the best-known commercial tannin extract, namely, the reaction of the mimosa tannin extract with 5% paraformaldehyde, over a range of different temperatures. The gel point was determined by three different methods, namely, by the crossover point of viscous and elastic moduli, by the extrapolation to ∞ of the zero-frequency viscosity, and by determining the point at which the value of $\tan \delta$ is constant whatever frequency is used in the measurement. The results obtained were critically compared. The comparisons obtained were good and were reproducible when the first two methods were used, but not when the third one was used. This allowed the determination of the energy of activation at different stages in the tannin–aldehyde polycondensation reaction and the calculation of the degree of con-

version of the tannin–aldehyde polycondensation before, at, and after the gel point. Mathematical expressions defining the degree of conversion for tannin–aldehyde reactions before, at, and after the gel point as a function of different moduli were developed and checked with the experimental data obtained. Methods and mathematical expressions for the determination of the rate constants of the different stages of the reaction were also developed and checked. After the gel point, the system was modeled using both a diffusion-controlled model and a second-order kinetic law. The applied results obtained indicated that, although a certain element of diffusion control is present, a second order, diffusion-independent kinetic is more valid under the experimental conditions used. This indicates that the rheometry approach to a polycondensation network is limited mostly by the capability of the equipment to the region after the gel point, where diffusion control does not as yet play a predominant role. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 852–863, 2002

Key words: rheology; tannins; resins; polycondensation; gelation; networks

INTRODUCTION

Commercial polyflavonoid tannin extracts have been produced and used industrially for many applications since the end of the 19th century.^{1,2} Among these uses is their relatively recent use as industrial wood adhesives,¹ which, perhaps, constitutes, today, the second most important bulk use of these materials other than for leather, although still far behind the latter. Their use as wood adhesives is based mainly on the reaction, gelling, and hardening of these very reactive, natural phenolic materials with formaldehyde. This is a polycondensation reaction similar but not completely equal to what was observed in synthetic phenol–formaldehyde resins.^{1,2} Considering the relevance of the rheological behavior of the tannin–formaldehyde reaction on their industrial application as ther-

mosetting wood adhesives, the literature is almost completely devoid of rheological studies on the gelling and hardening of these materials, other than some recent ones using thermomechanical analysis to follow hardening of the resin *in situ* on the substrate.^{3–6} Recently, a study on the rheology of water solutions of commercial tannin extracts was presented.⁷ Although some interesting and valuable information was obtained on the effects of pH and concentration on the rheological characteristics of various commercial tannins, this study was, however, rather limited as it did not extend to the reaction of these tannin extracts with formaldehyde. This study, hence, did not address the rheological characteristics of the formaldehyde-induced hardening reaction of industrially manufactured tannin extracts of different types and of the tannin extracts which are indeed used in industrial application as wood adhesives.

In this and the following article, the rheological characteristics of the reaction with formaldehyde of four commercial polyflavonoid tannin extracts, extracted under standard conditions, and of industrial

Correspondence to: A. Pizzi.

tannin extracts modified for different adhesive applications were investigated and compared. In this first part, the validity of some modifications of known methods was checked on the best-known commercial tannin extract.

EXPERIMENTAL

Water solutions of commercial polyflavonoid tannin extracts of mimosa (*Acacia mearnsii*) bark tannin extract, natural quebracho (*Schinopsis balansae*) wood tannin extract, pine (*Pinus radiata*) bark tannin extract, and pecan (*Carya illinoensis*) nut membranes tannin extract and, furthermore, a quebracho tannin extract modification from which all carbohydrates had been eliminated (quebracho QS) by organic solvent extraction and a quebracho tannin adhesive intermediate treated according to viscosity-reducing and reactivity-enhancing techniques already reported, the origins of which were, respectively, from Brazil, Argentina, Chile, United States, Italy, and, again, Argentina, were prepared, respectively, at a 50, 42, 35, 36, 45, and 45% extract solids concentration in water. The tannin extracts are produced industrially by countercurrent extraction with just water at 95°C in the case of mimosa, by countercurrent extraction with, respectively, 5 and 2% sodium sulfite and at 100 and 70°C for quebracho and pine tannin extracts, respectively, and by countercurrent extraction with 2–4% sodium sulfite and 0.4% sodium carbonate for pecan nut tannin extract. The industrially spray-dried tannin extracts were guaranteed at a percentage tannin (defined as the phenolic fraction of the extract containing trimers and higher oligomers as defined by the hide power test method) content of 75, 75, 72, 80, 96, and 75% for mimosa, quebracho, pine, pecan, carbohydrate-free quebracho (QS), and a modified quebracho adhesive intermediate, respectively, and all except quebracho QS contained carbohydrate oligomers and monomers, although at different amounts.^{1,8–15} Ninety-six percent paraformaldehyde fine powder was used as a hardener at the 5, 8, and 12% level solids on tannin extract solids. Mimosa and quebracho tannins are composed mainly of mixtures of prorobinetinidins and profisetinidins, while pine tannin is almost exclusively composed of procyanidins and pecan nut tannin is composed very predominantly of prodelfinidins and some procyanidins. Due to the widely different tannin viscosities, the values of $[A_0]$ used for the rate constants before the gel point were of, respectively, $[Tannin_0] = 0.595$ mol/L for all the mimosa tannin cases, 0.250 and 0.317 mol/L for pine and pecan tannin extracts, respectively, and 0.314, 0.355, and 0.339 mol/L, respectively, for natural quebracho tannin extract, quebracho QS, and quebracho tannin adhesive intermediate.

The solutions were tested with a Rheometrics controlled stress rheometer RS-500 with parallel-plate geometry for all the measurements; the plate diameter used was 40 mm and the gap in between the parallel plates was 0.3 mm. A humidity cover plus solvent trap based on a film of silicone oil applied to the perimeter of the plates were used to prevent solvent evaporation.

During oscillatory rheological measurements, shear was applied sinusoidally at a deformation amplitude (γ_{\max}) of 5%—hence, sufficiently weak not to destroy the structure of the gel or of the network which forms as the tannin–formaldehyde reactions proceeds. For each tannin, the measurements were repeated at four to five different temperatures and at five different frequencies, 2, 4, 6, 8, and 10 rad/s, to yield a series of 20–25 curves for each tannin–formaldehyde mix. From these measurements, the in-phase elastic modulus G' , the out-of-phase viscous modulus G'' , the complex modulus G^* , and the complex viscosity η^* (η^* is the vectorial sum of the dynamic viscosity elastic and loss components and a measure of the general resistance of a material to flow as a function of the stress rate) were obtained. Their values extrapolated to zero frequency were used. The measurements at five different angular frequencies, $\omega = 2, 4, 6, 8,$ and 10 rad/s, at each temperature, correspond at each defined time t to five values of viscosity, which, reported as a function of the frequency, allow the calculation by linear regression of the viscosity at zero frequency η_0^* , obtained by the value of the intersection on the y -axis. The moduli at zero-frequency G_0' , G_0'' , and G_0^* were also obtained in the same manner during the whole polycondensation reaction, before and after the gel point. The coefficients of correlation of these linear regressions were never lower than 0.94.¹⁶

The viscosity extrapolated at zero frequency was used because the viscosity is frequency (i.e., shear rate)-dependent. This was done, as explained in several texts^{17–22} and clearly stated in one of them,²² so that the gel point can be determined experimentally as a moment when the reactive system loses the possibility to flow. It is evident that this moment depends on the intensity of deformation of the material; moreover, the higher the shear rate, the earlier the cessation of flow of the curing material is recorded. As a rule, a total viscosity profile during gelation can be obtained with the shear rate variation within a few orders of magnitude and the moment of achieving the gel point is determined for the minimum shear rate. For the most exact determination of the gel time by the viscometry method, it is necessary to carry out experiments at several shear rates (i.e., frequencies) with the subsequent extrapolation to the zero rate.²²

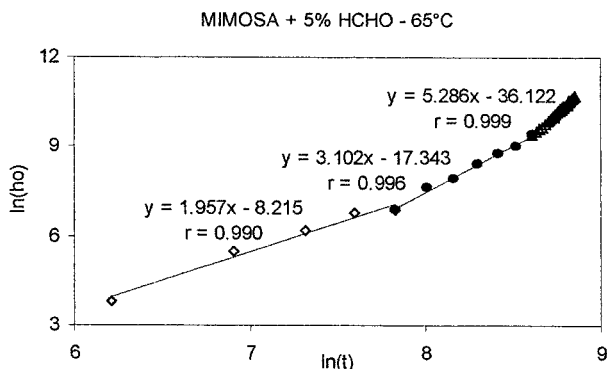


Figure 1 Graph in $\ln \eta_0$ and \ln time of the increase in viscosity as a function of time of the system mimosa tannin extract (prorobinetinidin tannin) + 5% paraformaldehyde during hardening at 65°C: (\diamond) stage 1, (\bullet) stage 2, and (\blacktriangle) stage 3, with linear slopes for the determination of coefficient a and coefficient of correlation r .

RESULTS AND DISCUSSION

Viscosity as a function of time

In the case of linear polymers, the viscosity is connected to the molecular mass by the expression

$$\eta = k^1 M_n^a \quad (1)$$

with η the viscosity, a and c constants, and M_n the molecular mass and where k^1 is a constant and $a = 1$ for $M < M_c$ or $a = 3.4$ for $M > M_c$, where M_c is the critical mass over which one has a change in the characters of the intramolecular linkages of the polymer.¹⁷ In the case of a polycondensation reaction, the main reaction phases can be observed by a graph of the log viscosity as a function of the log of the reaction time, each linear section of the graph corresponding to a different reaction phase.¹⁸ As the time increases, the molecular mass increases as the polycondensation goes on, forming longer polymer chains, which means, from eq. (1), that viscosity also increases. In the ideal case in which diffusional problems do not occur, the slope of the straight lines expressing the dependence of the viscosity on the reaction time increases from ≈ 1 ($t < t_c$) to ≈ 3.4 ($t > t_c$), t_c being the time when the system reaches the critical mass M_c .^{19,20} In the case of real reactions, and not of the ideal case, a time t_p is reached at which the viscosity increases very markedly and $a > 10$. In the case of the reaction of the mimosa tannin extract with 5% paraformaldehyde determined by extrapolation at zero frequency, graphs of $\ln \eta_0$ as a function of $\ln t$ were obtained for each temperature tested.

An example is shown in Figure 1, and the values of the slope coefficient a and coefficient b obtained for the different polycondensation phases before the gel point are shown in Table I. The results in Table I show several trends: (i) An increase in the reaction temper-

ature results in a clear decrease in the value of coefficient a in phase 3 of the reaction. This means that the degree of polymerization increases more slowly the higher is the reaction temperature. This can be explained by early network immobilization due to the existence of reaction diffusional problems after the gel point: The higher the temperature, the earlier and more marked is early network immobilization and the lower is the slope in the graph. (ii) With the exception of the 65°C case, a similar trend for coefficient a is also noticeable in phase 1, but this is due to different reasons. Here, such a trend is due to the increase in the limit value M_c , which is needed for entanglement with an increase in temperature in the early stages of the reaction—hence, when only small oligomers are present: at higher temperature then $a \approx 1$; when at lower temperature, the same low mass oligomers give a higher viscosity simply because the limit value M_c is lower. (iii) This is not anymore valid for phase 2 as a network has already started to form and the increase in the value a of the slope indicates a progressive increase in the value a of the slope indicates a progressive increase in gel formation with increasing temperature. (iv) It must also be noted that the scheme as shown in Figure 1, in which the three phases all have slopes higher than the preceding one, is not the most common case (Table I). In general, the slope of phase 2 is lower than the preceding one. This means that, in phase 2, the increase of the viscosity at zero frequency slows down.

This is an interesting phenomenon which will be dealt with in greater detail when looking at the kinetics of the tannin–formaldehyde reaction. It is possible, however, to advance some opinion on this behavior:

1. As the formation of linear polycondensates advances, it becomes progressively and statistically more difficult to maintain linear chain

TABLE I
Coefficients a and b at Different Temperatures of the Linear Correlation of $\log(\eta_0)$ Versus $\log(t)$ for the Reaction of Mimosa Tannin Extract + 5% Paraformaldehyde, for the Three Phases of the Reaction (see Fig. 1)

Phases	$\log(\eta_0)$ versus $\log(t)$				
	$y = ax + b$				
	Temperature (°C)				
	65	70	75	80	85
Phase I					
a	1.957	3.007	2.587	1.513	0.880
b	-8.215	-13.869	-8.202	-2.692	1.513
Phase II					
a	3.102	1.861	1.500	2.710	3.490
b	-17.343	-5.969	-1.412	-9.565	-12.147
Phase III					
a	5.286	4.472	3.042	3.854	2.311
b	-36.122	-26.633	-12.841	-16.365	-4.843

growth, leading to diffusional control for a chain end to find a chain end and to a slowdown in the increase of the viscosity. The increase in the slope intervening again in phase 3 corresponds to a change in the type of reaction occurring, namely, it is the phase in which branching starts and where, hence, reaction does not need to occur only end to end.

- This behavior could also stem from two competing reactions characteristic of any phenol-formaldehyde resin system.^{3,4} In the first networks formed, a considerable number of methylene ether bridges $-\text{CH}_2\text{OCH}_2-$ occur, which rearrange with relative ease to methylene $-\text{CH}_2-$ bridges with liberation of formaldehyde. This well-known reaction of depolymerization competes with the proceeding of the polycondensation and will, in total, yield a general slowdown in the rate of the viscosity increase. The second step of this rearrangement corresponds to the subsequent reaction of the liberated formaldehyde with the phenolic nuclei of the tannin, a reaction which does not subtract but, rather, reinforces the viscosity increase action of the polycondensation. The time values where both effects occur correspond to the times obtained for these effects through different analysis routes,²¹ indicating that this effect does at least contribute to the trend observed.

Instantaneous energy of activation

On considering the curing process at times far from the diffusion control part of the process, the rate of a kinetically controlled reaction can be expressed by an Arrhenius law:

$$\frac{dp}{dt} = kg(p) = k_0 \exp\left(-\frac{E}{RT}\right)g(p) \quad (2)$$

where p is the degree of conversion; k , the reaction rate constant; k_0 , the Arrhenius preexponential factor; E , the activation energy; and $g(p)$, the conversion-dependence function. By rearranging and integrating the above equation ($p = 0$ when $t = 0$), for a time t and a degree of conversion p , we get

$$\ln t = \frac{E}{RT} + \left[\ln \int_0^p \frac{dp}{g(p)} \right] - \ln k_0 \quad (3)$$

At a determined degree of conversion, the terms in the square brackets are constant. The equation can therefore be expressed as

$$\ln t = A + \frac{E}{RT} \quad (4)$$

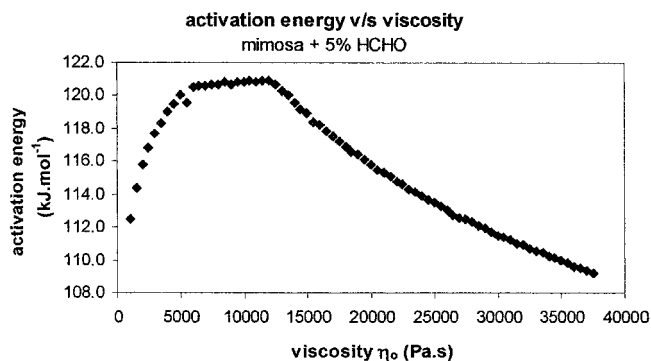


Figure 2 Variation of the activation energy as a function of the zero-shear viscosity for the system mimosa tannin extract (prorobinetinidin tannin) + 5% paraformaldehyde during hardening.

where A is only a function of p (i.e., of the zero shear viscosity, as this parameter is exclusively a function of the degree of conversion), with p the degree of conversion, t the time, k the kinetic constant, $g(p)$ the conversion-dependence function, k_0 the Arrhenius preexponential factor, E the activation energy, R the gas constant, T the temperature, and A the Arrhenius constant.

From the equations in Table I, it is possible to calculate at each temperature the time needed for the reaction to advance to yield a given value of viscosity. For instance, a viscosity of 20,000 Pa s is reached in 6103, 3544, 1775, 1190, and 591 s at, respectively, 65, 70, 75, 80, and 85°C. The reaction times so obtained allow calculation of the instantaneous energy of activation of the polycondensation by reporting on a graph $\ln(t)$, t being the reaction time, versus $1/RT$, the slope of the straight line so obtained representing the value of the energy of activation of the system. In the case at hand of mimosa tannin + 5% paraformaldehyde, the energy of activation is 115.8 kJ/mol.¹⁶ This calculation can be repeated to follow the progress of the polycondensation reaction—hence, for progressively higher values of the viscosity value extrapolated at zero frequency, in the 50–40,000 Pa.s range, to follow the variation of the instantaneous energy of activation during the whole reaction from the start of the formation of linear chains to the formation of the final hardened, crosslinked network. The variation of the value of the instantaneous energy of activation of the reaction of the mimosa tannin extract with 5% paraformaldehyde is shown in Figure 2.

In Figure 2, three distinct reaction phases can be observed:

- A first phase of rapid increase of the instantaneous energy of activation can be noticed at the beginning of the reaction at low viscosity. The activation energy increases 8% from 112 to 121 kJ/mol, for a viscosity increase to 6000 Pa s. In

this phase, as pointed out previously, the increase in viscosity is caused by the linear growth of the polymer chains present. As the reaction proceeds and the relative number of end reactive sites decreases, the probability of an end-to-end reaction becomes much lower and the viscosity much higher, adding a diffusional problem to the simple statistical decrease of its probability. Maintaining linearity of the chains becomes then progressively more difficult, and, hence, as the reaction proceeds, the instantaneous energy of activation increases (Fig. 2).

- The second phase in Figure 2 is characterized by the appearance of a plateau at the 121 kJ/mol value of the instantaneous energy of activation, this plateau being maintained from a viscosity of 6000 Pa s to a viscosity 13,000 Pa s. This indicates a change in the type of reaction occurring, namely, the formation of branched rather than just linear oligomers. The number of available reactive sites on a chain increases as all the sites along the length of the chains can now react. Thus, the reaction is statistically more favorable and not diffusion-controlled anymore.
- The third phase in Figure 2 shows a steady decrease in the instantaneous energy of activation starting from a viscosity of around 13,000 Pa s. In this phase, the proportion of branched oligomers increases to eventually form a gel and then a covalent crosslinked network, and, hence, one would rather expect an increase in the energy of activation. In reality, the trend in Figure 2 is caused by the method used to calculate the energy of activation, being based exclusively on the viscosity of the system—hence, on the part of the system which is in solution. Thus, the third phase in Figure 2 just represents the variation of the energy of activation of only the sol part of the system and not of the sol + gel total. At 13,000 Pa s, the gel starts to form and the proportion of the sol fraction decreases, and while the energy of activation of just the sol remains the same, the instantaneous energy of activation of sol + gel decreases as the material, which forms the gel, disappears from the solution.

Determination of the gel point

The gel point can be determined by rheometry according to three different systems,²² and all three have been tried on the reaction of the mimosa tannin extract with 5% paraformaldehyde. The first method places the gel point at the intersection of the elastic and viscous moduli G' and G'' . To eliminate the dependence of G' and G'' on the frequency, the values G_0'

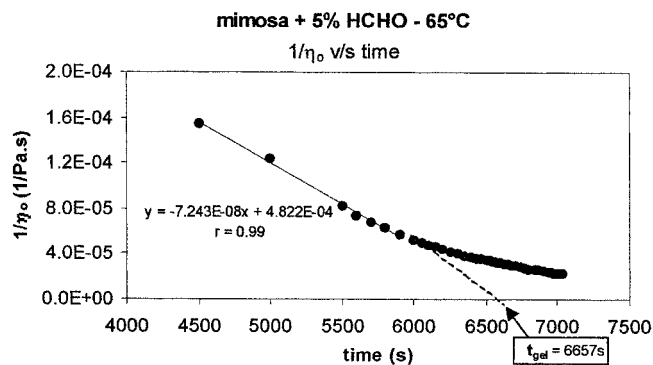


Figure 3 Second method ($1/\eta_0 \rightarrow 0$) for the determination of the gel point. Variation of $1/\eta_0$ as a function of time of the system mimosa tannin extract (prorobinetinidin tannin) + 5% paraformaldehyde during curing at 65°C.

and G_0'' extrapolated to zero frequency were the ones used.

The second method relies on the tendency of $M_w \rightarrow \infty$; hence, viscosity $\rightarrow \infty$ at the gel point. The method consists then to extrapolate to ∞ the values of the viscosity at zero frequency ($\eta_0 \rightarrow \infty$ or, better for practical reasons, $1/\eta_0 \rightarrow 0$). The values of the zero-frequency viscosity used in this method are those obtained by extrapolating to zero frequency the parameters measured at 2, 4, 6, 8, and 10 rad/s. The application of this method for the case of the reaction of mimosa tannin extract with 5% paraformaldehyde is shown in Figure 3. The gel point (Fig. 3) is defined as the intersection with the x -axis of the prolongation of the linear part of the regression.

The third method is based on the principle that since the gel point depends only on the temperature it is then independent of the frequency at which the measures are done.²³ By tracing graphically the five frequencies used, the variation of $\tan \delta (= G''/G')$ as a function of the time, the gel point is defined as the intersection of the five curves obtained: thus, the point where the value of $\tan \delta$ is constant whatever the frequency used in the measurements [$\tan \delta \neq f(\omega)$]. While this method is theoretically acceptable, it has been shown to be almost impossible to apply consistently to the condensation of a complex, mixed natural material such as polyflavonoid tannin extract. In the best case, for example, of the reaction of mimosa tannin + 5% paraformaldehyde at 80°C, four curves do, indeed, cross at the same point, but the fifth does not. The gel point obtained is reported in Table II. In all other cases, there are several points of crossing of the curves with, at best, three curves crossing (and often only two). This leads, at best, to three and sometimes to four possible points being candidates in which $\tan \delta \neq f(\omega)$. None of them is near to what was observed with the other methods and, consequently, this method had to be discarded after checking its validity

TABLE II
Comparison of Gel Times Obtained by Three Different
Methods for the Mimosa Tannin Extract + 5%
Paraformaldehyde System.

Method	Gel times (s)				
	Temperature (°C)				
	65	70	75	80	85
Method 1	6625	3730	2275	1285	745
Method 2	6657	3680	2250	1275	760
Difference (%)	0.5	1.4	1.2	0.8	2.0
Method 3	—	—	—	1063	—

Method 1: $G' = G''$. Method 2: $1/\eta_0 \rightarrow 0$. Method 3, $\tan \delta = \text{constant}$ when varying the applied frequency.

(or lack of it) for all the tannins tested (all the results on this and other methods are stored in ref. 16).

The values of the gel time obtained with the different methods outlined are comparable and are shown in Table II. For the calculation of the physicochemical properties of the gel and of the network after the gel point and to calculate the degree of advancement of the reaction, the method $G' = G''$ was used, while both methods were used for the advancement of the reaction before the gel point.

It is of interest to note in Table II the marked effect of the reaction temperature on the gel time. The relationship between the gel time, expressed as $\ln(t_{\text{gel}})$, as a function of the inverse of the reaction temperature $1/T$, is linear and the slope of the straight line allows calculation of the energy of activation of the tannin + formaldehyde reaction at the gel point (Fig. 4). The difference between the energy of activation at the gel point calculated from the values of the gel time obtained with the first and second method in Table II is small: 109.3 kJ/mol from the first method and 108.6 kJ/mol from the second method. These values compare favorably with the energies of activation of the same reaction obtained previously by measuring the rate of disappearance of formaldehyde in the reaction.²¹

Calculation of the degree of conversion p

In the calculation of the degree of conversion, three different situations need to be examined: before the gel point, at the gel point, and after the gel point.

Before the gel point

The degree of conversion of the tannin-formaldehyde reaction is calculated from the viscosity. In the case of polydisperse polymers, eq. (1) still applies, but it has been shown that the zero-frequency viscosity η_0 can be represented by eq. (5)²⁴:

$$\eta_0 = k C^b (M_n C)^a \quad (5)$$

where C is the concentration of polymer and b is a constant ($b \approx 1.25$).

At the gel point, η_0 has, generally, a finite value. At a given time t , the ratio of η_0 and $(\eta_0)_g$, the value of η_0 at the gel point, is related through the equation

$$\frac{\eta_0}{(\eta_0)_g} = \left(\frac{C}{C_g}\right)^{a+b} \left(\frac{M_n}{M_{ng}}\right)^a \quad (6)$$

As the polymer concentration is directly proportional to a polycondensation degree of conversion, one can substitute the ratio C/C_g in eq. (6) by the ratio of degrees of conversion p/p_g to obtain eq. (7):

$$\frac{\eta_0}{(\eta_0)_g} = \left(\frac{p}{p_g}\right)^{a+b} \left(\frac{M_n}{M_{ng}}\right)^a \quad (7)$$

M_n is defined by eq. (8)²⁵:

$$M_n = M_0 \frac{1+r}{1+r(1-2p)} \quad (8)$$

where M_0 is the molecular mass of the polymer repeating unit; r , the molar ratio of the reagents reactive groups; and p , the degree of conversion.

From eqs. (7) and (8), it is possible to obtain an equation correlating the zero-frequency viscosity η_0 and the degree of conversion p of the reaction (eq. (9)):

$$\frac{\eta_0}{\eta_{0g}} = \left(\frac{p}{p_g}\right)^{a+b} \left(\frac{1+r-2p_g r}{1+r-2pr}\right)^a \quad (9)$$

a and b are constants and the index g refers to the value at the gel point of the relevant parameters. Equation (9) allows, then, determination of the degree of conversion p at any time t ($t \leq t_{\text{gel}}$), as all the other parameters are obtainable or known: The zero-frequency viscosity values are measured experimentally; the reactive groups molar ratio r is defined at the start, as the concentrations of tannin and formaldehyde are fixed at the beginning; and p_g at the gel point can be calculated using eq. (10). In eqs. (2)–(6), η_0 is the zero

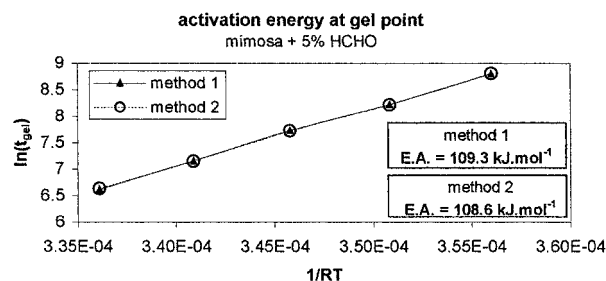


Figure 4 Calculation of the energy of activation for the system mimosa tannin extract (prorobinetinidin tannin) + 5% paraformaldehyde starting from the values of the gel time at 65, 70, 75, 80, and 85°C: (▲) method 1; (○) method 2.

shear viscosity; $(\eta_0)_g$, the zero-shear viscosity at the gel point; a , b , and c , constants; C , the concentration of the polymer; M_n , the molecular mass of the polymer; $(M_n)_g$, the molecular mass of the polymer at the gel point; M_0 , the molecular mass of polymer repeating unit; p , the degree of conversion; p_g , the degree of conversion at the gel point; and r , the molar ratio of the reagents reactive groups.

At the gel point

For a polycondensation reaction, the gel point can be forecasted by several equations,²⁵⁻²⁷ but one of the simpler and easier to use is²⁵

$$p_g = \frac{1}{\sqrt{r(f_{WA} - 1)(f_{WB} - 1)}} \quad (10)$$

where p_g is the degree of conversion at the gel point; r , the molar ratio of the reagents reactive groups which must always be maintained at ≤ 1 , and f_{WA} and f_{WB} , the functionalities here of the tannin and of formaldehyde. For the mimosa tannin + 5% paraformaldehyde, the values of these parameters used to calculate p_g were the average DP_n of mimosa tannin = 4.9 (refs. 28-30) and, hence, an average functionality of 5.9,^{1,16,29,30} a formaldehyde functionality = 2, r calculated to be 0.949, and the value of p_g obtained as 0.464.

After the gel point

A method to calculate the degree of conversion after the gel point was recently proposed in studies of synthetic polycondensation resins.³¹⁻³³ This method is based on the concept that the equilibrium modulus G'_0 (determined by extrapolating to zero frequency the values of the elastic modulus G') is proportional to the crosslinked density of the network which has formed, the crosslinked density depending on the advancement of the reaction. This infers that the increase in the degree of conversion is proportional to the increase in the equilibrium modulus (eq. (11)):

$$\frac{p - p_g}{1 - p_g} \propto \frac{G - G_g}{G_\infty - G_g} \quad (11)$$

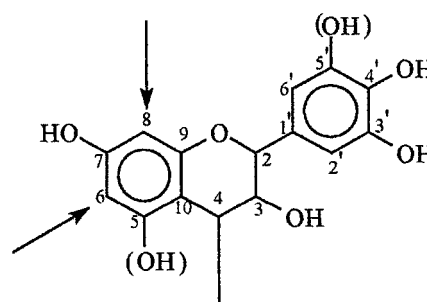
where the value of the parameters indexed g are their values at the gel point and G_∞ is the equilibrium modulus corresponding to $p_\infty = 1$.

The original approach envisaged that, since each crosslinking node is formed from three chains joining, an exponent of 1/3 is necessary in eq. (12),

$$p = p_g + (1 - p_g) \left(\frac{G - G_g}{G_\infty - G_g} \right)^{1/3} \quad (12)$$

While this approach is correct in the case of synthetic polycondensation polymers, the use of eq. (6) is rather problematic in the case of the reaction of polyflavonoid tannins with formaldehyde. These problems deserve a more in-depth discussion:

1. The first point concerns the use of the 1/3 exponent. The original approach that each crosslinking node is formed from three chains joining is not strictly valid in the case of the reaction of tannins with formaldehyde. This approach is valid strictly if one considers the tannin as composed of monomers presenting three available reactive sites, namely, C6 and C8 being reactive with formaldehyde and C4 joining directly with another flavonoid unit:



The problem which is generated by defining the monomer as a single, unbound flavonoid unit is that this does not take into account the existence of the interflavonoid linkages C4→C6 and C4→C8 which connect the units in a natural tannin. In the calculation of the p_{gel} , it is, rather, the average oligomer, of $DP_n = 4.9$, which is the only one which can be safely defined as the monomer as regards the reaction with formaldehyde. Thus, in the case of such a macromonomer, in extrapolating to the level of the single flavonoid unit, two sites are already used to form the interflavonoid linkage with the units that precede and that follow and, hence, unavailable for reaction with formaldehyde. The concept of a three-chains node is not strictly applicable in such a context.

2. The second point of concern as regards eq. (12) deals with G_∞ . From eq. (12), G_∞ corresponds to a degree of conversion $p = 1$ —hence, with the reaction being totally completed. In this context, G_∞ is the modulus of the final, completely crosslinked covalent network. However, it is not possible to measure by rheometry the modulus of the final, completely crosslinked covalent network as the equipment measures for torsion couples in the 0.1–200 g.cm range. In the numerical solutions of eq. (12) is, in reality, the value of G , which corresponds to the maximum

value of the torsion couple that the rheometer is capable of measuring, which is taken as G_∞ . The real values of G_∞ will be higher than those measured. In eq. (12), if G_∞ increases, then p also increases. Thus, the values of the degree of conversion p obtained experimentally, taking for G_∞ the max value measurable rather than the real value of G_∞ , will be overvalued.

- The third point is that the use of the equilibrium modulus G'_0 in eq. (12) is, at best debatable. The justification for this is that, by definition, after the gel point, $G'_0 > \text{to } \geq G''_0$, and, hence, it is better to use G'_0 in eq. (12). However, for practical reasons, the solutions of tannin in this study are in the 35–50% range (these being the highest solution concentrations used in industrial application). The proportion of solvent and water is then very high and this markedly affects polycondensations. After the gel point, the gel that starts to predominate in the initial part of the reaction, after gelling the sol and the solvent, is present in a considerable amount and influences considerably the response of the system. The complex modulus G^* defined as $G' + iG''$ takes in consideration the total system—thus, the gel, sol, and solvent. Furthermore, equally conveniently, the contribution of G'' to G^* decreases as the reaction advances, reproducing exactly the decrease in importance of the sol fraction as a function of the advancement of the reaction. The question arises then if it would not be better to rely on G_{0^*} extrapolated at zero frequency rather than on $G_{0'}$ as in eq. (12).

To answer this question in the case of mimosa tannin extract + 5% paraformaldehyde, eq. (12) was solved both with and without the 1/3 exponent and using all the three zero-frequency moduli, namely, G_{0^*} , $G_{0'}$, and $G_{0''}$. This was done for all the five temperatures of the reaction. In Figure 5 are reported the results for the case at 70°C, the other cases giving similar results (see ref. 16, the repository of the other results). In Figure 5 are shown an increase in the degree of conversion p before the gel point [calculated by eq. (9)]; the values p' , p'' , and p^* of the degree of conversion after the gel point calculated by means of eq. (12) using $G_{0'}$, $G_{0''}$, and G_{0^*} , respectively, are presented, and all these with and without the 1/3 exponent in eq. (12). In general, the differences among p' , p'' , and p^* are minimal, with the exception of what is shown in Figure 5, where it becomes quite evident that p^* without the 1/3 exponent describes much better the total system after the gel point. The use of the 1/3 exponent is clearly shown not to be usable in the case of the tannin case, as, for example, in the case at 75°C,¹⁶ the degree of conversion passes from 0.464 at the gel point to 0.853 in 25 s (or from 0.464 to 0.8 in 8 s

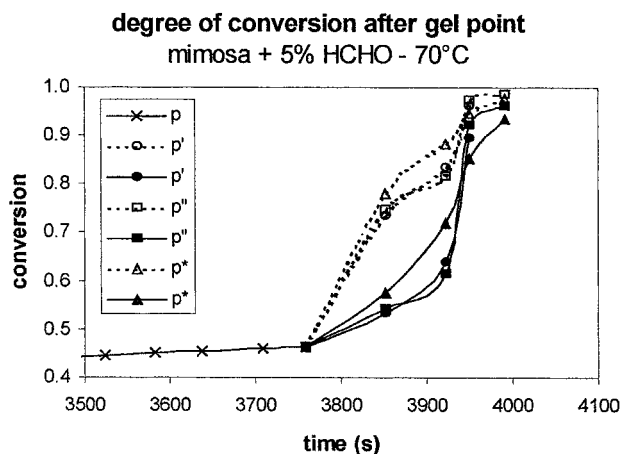


Figure 5 Comparison of different methods of calculation of the degree of conversion p after the gel point for the system mimosa tannin extract (prorobinetinidin tannin) + 5% paraformaldehyde during hardening at 70°C: (×) p before the gel point, (○) p' , (□) p'' and (Δ) p^* according to eq. (9) and (●) p' , (■) p'' , and (▲) p^* according to eq. (10).

in the case in Fig. 5). An increase of p of 85% in such a short time, with the diffusional hindrance, which is always present in this type of reactions, is not really acceptable. After the gel point, it would be expected to see a much sharper slope for the increase of p but not of the order of an almost vertical straight line. The curves based on the equation without the 1/3 exponent appear to be closer to reality with still a very rapid but more moderate increase of p , followed by a slowing down of its growth due to the appearance of diffusional problems at degrees of conversion higher than 0.9, confirming a limit already determined by TTT diagrams built using different techniques.^{6,34,35}

In the case of the reaction of a polyflavonoid tannin and formaldehyde, it is then eq. (13) which needs to be used for the calculation of the degree of conversion p after the gel point:

$$p = p_g + (1 - p_g) \left(\frac{G_0^* - G_{0,g}^*}{G_{0,\infty}^* - G_{0,g}^*} \right) \quad (13)$$

with p the degree of conversion, p_g the degree of conversion at the gel point, G the equilibrium modulus at time t , G_g the equilibrium modulus at the gel time, G_∞ the equilibrium modulus corresponding to $p_\infty = 1$, and G^* the complex modulus.

The remark concerning G_∞ in eq. (9) is equally valid for $G_{0,\infty}^*$ in eq. (13). Thus, the values of $G_{0,\infty}^*$ used to calculate p are the highest measurable values of $G_{0,\infty}^*$, the rheometer limitations not allowing calculation of the complex modulus of the completely crosslinked, final network. This means that the values of p obtained with this method are always slightly higher than what they are in reality. It is thus necessary to always keep in mind that the calculated values of p are relative, that

the last measurement does not correspond to the final totally crosslinked network, and that the reaction does continue beyond the limits imposed by this experimental limitation.

Kinetics

Before the gel point

With p being the degree of conversion and r the molar ratio, r can be taken as the ratio of the initial concentrations of the two reagents $[A_0]/[B_0]$, and $[A]$ and $[B]$, the concentrations at a time t , by applying a second-order kinetic law equation $-d[A]/dt = -d[B]/dt = k[A][B]$, we obtain an equation having as sole variables t and p (eq. (14))¹⁶:

$$\frac{dp}{dt} = k[A_0] \frac{(1-p)(1-rp)}{r} \quad (14)$$

which by integration yields eq. (15):

$$t_2 - t_1 = \frac{r}{k[A_0](1-r)} \times \left[\ln\left(\frac{1-rp_2}{1-p_2}\right) - \ln\left(\frac{1-rp_1}{1-p_1}\right) \right] \quad (15)$$

As the degree of conversion was calculated from the variation of the viscosity at zero frequency at different reaction times, the value of the kinetic constant k can be calculated graphically by tracing the curve $t = f(p)$. Thus, for each temperature studied, by reporting on the x -axis the difference,

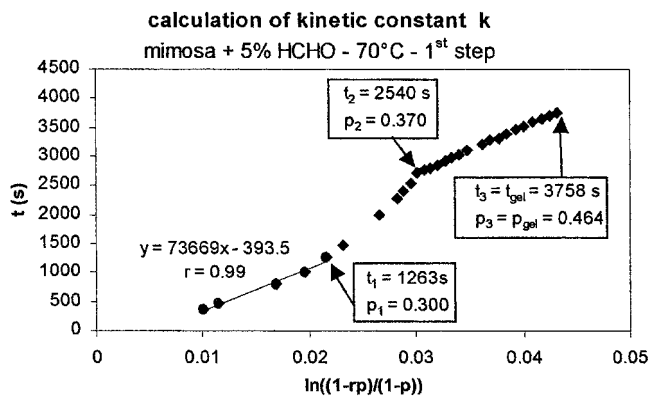


Figure 6 Determination by graphic methods of the rate constants k_1 , k_2 , and k_3 of the three successive second-order reaction zones for the system mimosa tannin extract (pro-robinetinidin tannin) + 5% paraformaldehyde at 70°C, characterizing the polycondensation reaction before the gel point. The (●) slope value of 73,669 allows the determination of the rate constant $k_1 = 2.53 \times 10^{-4}$ L/(mol × L). This and the (◆) values for the other two zones are reported in Table III.

TABLE III
Rate constants k_1 , k_2 , and k_3 in $\text{L mol}^{-1} \text{s}^{-1}$ and Activation Energies of the Three Distinct Reaction Phases of the Mimosa Tannin Extract + 5% Paraformaldehyde Polycondensation Before the Gel Point

	Temperature (°C)					Activation energy (kJ/mol)
	Before the gel point	65	70	75	80	
$k_1 (\times 10^{-4})$	1.50	4.25	9.48	7.82	12.3	97.4
$k_2 (\times 10^{-4})$	—	1.95	2.96	—	18.7	158.6
$k_3 (\times 10^{-4})$	2.57	3.73	4.49	10.0	10.9	78.0

$$\ln\left(\frac{1-rp_2}{1-p_2}\right) - \ln\left(\frac{1-rp_1}{1-p_1}\right)$$

and on the y -axis the time, the value of k is calculated from the slope according to eq. (16):

$$k = \frac{r}{\text{slope} \cdot [A_0](1-r)} \quad (16)$$

with $[A]$, $[B]$ the concentration at time t of the two reagents, $[A_0]$, $[B_0]$ the initial concentration at time $t = 0$ of the two reagents, p the degree of conversion, r the molar ratio of reagents reactive groups, and k the kinetic constant ($\text{L mol}^{-1} \text{s}^{-1}$).

In Figure 6 is shown the case of the reaction of mimosa tannin + 5% paraformaldehyde at 70°C, where it is clearly shown that before the gel point this polycondensation can be modeled in three successive steps, with each step responding to a second-order kinetic law. The values of the second-order kinetic constants k_1 , k_2 , and k_3 obtained in this manner, and of the corresponding activation energies for all the different reaction temperatures for the mimosa tannin + 5% paraformaldehyde reaction, are shown in Table III. Both Figure 6 and Table III indicate that, after the first reaction step, the reaction slows down at p_1 , entering the second reaction step and accelerates again at p_2 , at the beginning of the third reaction step.

The same two reasons already presented for the temporary slowing down of the increase of the viscosity can also be advanced here to explain the slowing down of the reaction observed in the second reaction step: (i) the statistical decrease of the probability of the reaction during the linear phase of growth of the polymer with the acceleration occurring once branched polymers start to be formed, and (ii) the presence of two competitive reactions, namely, the decomposition of the methylene ether bridges formed competing with the forward polycondensation reaction and predominating for a limited period of time.

After the gel point

After the gel point, the kinetics of the reaction can be dealt with either on the basis of a second-order kinetic

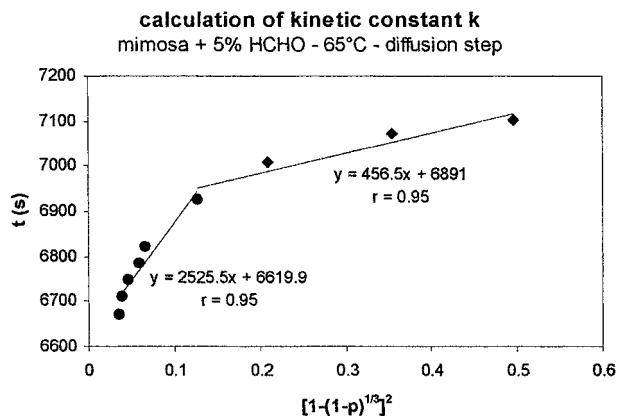


Figure 7 Determination by graphic methods according to the diffusion model of Jander of the rate constants k_4 and k_5 of the two reaction zones for the system mimosa tannin extract (prorobinetidin tannin) + 5% paraformaldehyde at 65°C, characterizing the polycondensation reaction after the gel point if the reaction is considered to be diffusion-dependent (see Table IV).

law or, alternatively, as a diffusion-controlled process by using as a model a diffusion equation, in this case, the model having been chosen was the equation of Jander.^{36,37} This was chosen as it is a model developed for solid-state reactions and, hence, used in our case after the gel point where the system is closer to a solid than to a liquid and progressively becoming closer to a solid. All the assumptions of Jander's^{36,37} equation (eq. (17)) are valid for the tannin-formaldehyde reaction:

$$t = \frac{1}{k} [1 - (1 - p)^{1/3}]^2 \quad (17)$$

where the rate constant k is defined as $k = 2D/R_0^2$, with D the diffusion coefficient and R_0 the concentration of the material not reacted at the start of the reaction. After the gel point, k can then be determined by tracing the reaction time t as a function of $[1 - (1 - p)^{1/3}]^2$ as shown in Figure 7 for the reaction under consideration at 65°C. The low number of experimental points due to the reaction rapidly reaching the physical limits of the rheometer sometimes also constitutes here a problem. For the case in Figure 7, there is a sufficient number of experimental points to be able to see that

there are two phases of the reaction after the gel point which correspond to rate constants k_4 and k_5 , which can be calculated. In other cases, especially at the higher reaction temperatures, the second phase is often so fast to start that the rate constant of the first phase cannot be calculated, as indicated by the results reported in Table IV. As the reaction advances after the gel point, one would expect to find rate constants progressively lower, indicating a diffusion-controlled slowing down of the reaction. This is not the case for the results in Table IV where the tendency is exactly the inverse. As (i) this trend is maintained for all other tannins and it is not then just due to experimental error and (ii) independent results by thermomechanical analysis for the same systems in contact with a substrate have indicated that the trend observed is the inverse of what is shown in Table IV, it is clear that the results observed in Table IV are an artifact of the calculation method used.

As the calculation method, due to the physical limits of the rheometer, overvalues the degree of conversion, it is quite likely that the last few measurements before the limits imposed by the rheometer is reached still correspond to the phase of networking which is not diffusion-controlled. If this is the case, it might be better to deal with the kinetics after the gel point by just using a second-order kinetic law model and not a diffusion-controlled one. The results of this alternative approach for the same case shown in Figure 7 are shown in Figure 8, and the results obtained for the rate constants are shown in Table V. These results show that the trend of the rate constants is similar to what was observed for the diffusion-controlled model; hence, $k_4 < k_5 < k_6$ and the correctness of the comparison ends here. The constants in Table V have much higher values. It is incorrect, of course, to compare first (Table III)- and second (Table V)-order constants' values relative to each other. The trends observed, however, confirm that the reaction phases studied after the gel point are still those where, while diffusion problems do clearly already occur and are not negligible, they are still relatively small. The high degree of conversion phase, where diffusion problems are predominant and very marked,^{35,38,39} appears then to occur well beyond the physical limits imposed by the equipment used, a fact confirmed, using different tech-

TABLE IV
Rate Constants k_4 and k_5 in s^{-1} and Activation Energies of the Two Distinct Reaction Phases of the Mimosa Tannin Extract + 5% Paraformaldehyde Polycondensation After the Gel Point When Calculated by a Diffusion-controlled Model

After the gel point-diffusion controlled model	Temperature (°C)					Activation energy (kJ/mol)
	65	70	75	80	85	
$k_4 (\times 10^{-4})$	3.96	4.57	—	11.4	—	72.8
$k_5 (\times 10^{-4})$	21.9	20.7	21.8	52.2	31.2	19.1

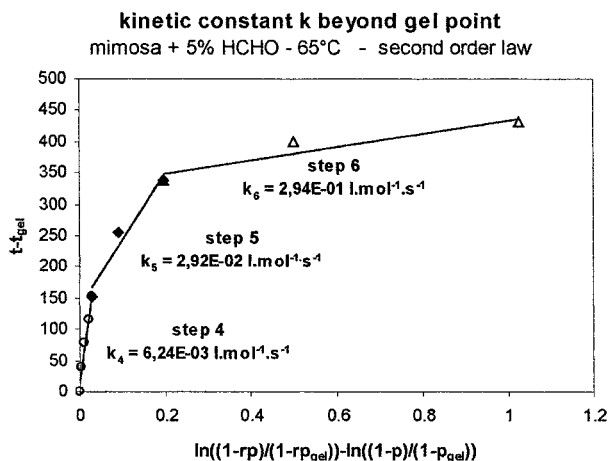


Figure 8 Determination by graphic methods according to a second-order law of the rate constants k_4 , k_5 , and k_6 of the three reaction zones for the system mimosin tannin extract (prorobinetinidin tannin) + 5% paraformaldehyde at 65°C, characterizing the polycondensation reaction after the gel point if the reaction is considered to be in the early phases of hardening and taken as not to be diffusion-dependent (see Table V).

niques, by recent findings on polycondensation resins on a substrate.³⁵

CONCLUSIONS

The reaction of a commercial polyflavonoid tannin extract of the prorobinetinidin/profisetinidin type with formaldehyde was studied by parallel-plate rheometry both before and after the gel point. To allow this, the validity of some modifications of known methods was checked on the best-known commercial tannin extract. By following the variation of zero-frequency viscosity as a function of the reaction time, it can be noticed that, before reaching the gel point, three well-distinct phases of the reaction can be noticed, related to well-defined occurrences at the molecular level, each phase presenting a well-defined value of the rate constant and a different energy of activation. The gel point was determined by three different methods, namely, by the crossover point of the viscous and elastic moduli, by the extrapolation to ∞ of the zero-frequency viscosity, and by determining the point at

which the value of $\tan \delta$ is constant whatever the frequency used in the measurement. The results obtained were critically compared. The comparisons obtained were good and were reproducible when the first two methods were used, but not when the third one was used. This allowed the determination of the energy of activation at different stages in the tannin-aldehyde polycondensation reaction and the calculation of the degree of conversion of the tannin-aldehyde polycondensation before, at, and after the gel point. Mathematical expressions defining the degree of conversion for tannin-aldehyde reactions before, at, and after the gel point as a function of different moduli were developed and checked with the experimental data obtained. Methods and mathematical expressions for the determination of the rate constants of the different stages of the reaction were also developed and checked. After the gel point, the system was modeled using both a diffusion-controlled model and a second-order kinetic law. The applied results obtained indicated that, although a certain element of diffusion control is present, a second-order, diffusion-independent kinetic is more valid under the experimental conditions used. This indicates that the rheometry approach to a polycondensation network is limited, mostly by the capability of the equipment, to the region after the gel point where diffusion control does not as yet play a predominant role.

NOMENCLATURE

a, b, c	constants
A	Arrhenius constant
$[A], [B]$	concentrations at time t of the two reagents (mol L^{-1})
$[A_0], [B_0]$	initial concentrations at time $t = 0$ of the two reagents (mol L^{-1})
C	concentration (mol L^{-1})
D	diffusion coefficient ($\text{m}^2 \text{mol}^{-1} \text{s}^{-1}$)
DP_n	number-average degree of polymerization
E	activation energy (kJ mol^{-1})
f_{WA}, f_{WB}	functionalities of the two reagents
$g(p)$	conversion-dependence function
G'	elastic/storage modulus (Pa)
G''	viscous/loss modulus (Pa)

TABLE V
Rate Constants k_4 , k_5 , and k_6 in $1 \text{ mol}^{-1} \text{ s}^{-1}$ and Activation Energies of the Three Reaction Phases of the Mimosin Tannin Extract + 5% Paraformaldehyde Polycondensation After the Gel Point During Network Formation When Calculated by a Second-order Kinetic Law

After the gel point—plain second-order law	Temperature (°C)					Activation energy (kJ/mol)
	65	70	75	80	85	
$k_4 (\times 10^{-3})$	6.24	13.7	67.1	32.3	12.0	136.5
$k_5 (\times 10^{-3})$	29.2	122.0	—	266.0	—	136.8
$k_6 (\times 10^{-3})$	294	—	—	—	—	—

G^*	complex modulus, $G^* = G' + G''$ (Pa)
G_0	modulus extrapolated at frequency zero (Pa)
G_g	modulus at gel point
G_∞	modulus corresponding at a degree of conversion $p_\infty = 1$
k	kinetic constant ($L \text{ mol}^{-1} \text{ s}^{-1}$ for a second-order model, s^{-1} for Jander's model)
k_0	Arrhenius preexponential factor
k^f	Mark-Houwink constant
M_n	number-average molecular mass of the polymer (g mol^{-1})
M_0	molecular mass of the polymer repeating unit (g mol^{-1})
M_c	critical molecular mass for entanglement (g mol^{-1})
n	critical relaxation exponent
p	degree of conversion
p_g	degree of conversion at gel point
r	molar ratio of the reagents reactive groups
R	gas constant
R_0	concentration of material not reacted at the start of the reaction (mol L^{-1})
S	gel stiffness (Pa s^n)
t	time (s)
t_{gel}	gel time (s)
T	temperature (K)
η	viscosity (Pa s)
η_0	zero-shear viscosity/viscosity extrapolated at frequency zero (Pa s)
η_g	viscosity at gel point (Pa s)
δ	phase displacement/loss angle (rad), $\tan \delta = G''/G'$
γ	applied sinusoidal shear strain $\gamma = \gamma_{\text{max}} \sin(\omega t)$; γ_{max} , strain amplitude
τ	sinusoidal shear stress $\tau = \tau_{\text{max}} \sin(\omega t + \delta)$; τ_{max} , stress amplitude
ω	frequency (rad s^{-1})
λ_0	relaxation time (s)

REFERENCES

- Pizzi, A. In *Wood Adhesives, Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; Vol. 1, Chapter 4.
- Collieri, L. *Le Fabbriche Italiane di Estratto di Castagno*; Milanostampa S.p.A.: Farigliano (CN), Italy, 1989.
- Garcia, R.; Pizzi, A. *J Appl Polym Sci* 1998, 70, 1083.
- Garcia, R.; Pizzi, A. *J Appl Polym Sci* 1998, 70, 1093.
- Garcia, R.; Pizzi, A.; Merlin, A. *J Appl Polym Sci* 1997, 65, 2623.
- Garnier, S.; Pizzi, A.; Vorster, O. C.; Halasz, L. *J Appl Polym Sci* 2001, 81, 1634.
- Garnier, S.; Pizzi, A. *J Appl Polym Sci* 2001, 81, 3220.
- Pizzi, A. *Advanced Wood Adhesives Technology*; Marcel Dekker: New York, 1994.
- Roux, D. G. In *Mimosa Extract*; Shuttleworth, S., Ed.; LIRI Leather Industries Research Institute: Grahamstown, South Africa, 1965, pp 33–51.
- Stephen, J. *J Chem Soc* 1951, 646.
- Roux, D. G. *J Soc Leath Trades Chem* 1952, 36, 274.
- Abe, I.; Funaoka, M.; Kodama, M. *Mokuzai Gakkaishi* 1987, 33, 582.
- Sealy-Fisher, V. J.; Pizzi, A. *Holz Roh Werkstoff* 1992, 50, 212.
- Pizzi, A.; Stephanou, A. *Holz Holzver* 1993, 45(2), 30.
- McGraw, G. W.; Rials, T. G.; Steynberg, J. P.; Hemingway, R. W. In *Plant Polyphenols*; Hemingway, R. W.; Laks, P. E., Eds.; Plenum: New York, 1992; pp 979–990.
- Garnier, S. *Doctoral Thesis, University Henri Poincaré-Nancy 1, Nancy, France, 2002* (All additional data not shown in this article are stored and easily accessible in this document).
- Vinogradov, G. V.; Malkin, A. Y. *Rheology of Polymers*; Springer-Verlag: Berlin, 1980.
- Naroditskaya, E. Y.; Khodzhaeva, I. D.; Kulichikhin, S. G.; Pozdnyakou, V. Y.; Yunitskii, I. N.; Kireev, V. V.; Malkin, A. Y. *Vysikomolek Soed B* 1985, 27, 713.
- Malkin, A. Y.; Kulichikhin, S. G.; Kozhina, V. A.; Bolotina, L. M. *Vysikomolek Soed A* 1987, 29, 418.
- Kulichikhin, S. G.; Demina, G. I.; Bokareva, E. Z.; Malkin, A. Y. *Plastmassy* 1980, 1, 57.
- Rossouw, D. duT.; Pizzi, A.; McGillivray, G. *J Polym Sci Chem Ed* 1980, 18, 3323.
- Malkin, A. Y.; Kulichikhin, S. G. *Adv Polym Sci* 1991, 101, 217–256.
- Winter, H. H.; Mours, M. *Adv Polym Sci* 1997, 134, 164–231.
- Pearson, D. S. *Rubb Chem Technol* 1987, 60, 439.
- Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991.
- Pizzi, A. *J Appl Polym Sci* 1997, 63, 603.
- Pizzi, A. *J Appl Polym Sci* 1997, 65, 1843.
- Pizzi, A. *Advanced Wood Adhesives Technology*; Marcel Dekker: New York, 1994.
- Fechtal, M.; Riedl, B. *Holzforschung* 1993, 47, 349.
- Thompson, D.; Pizzi, A. *J Appl Polym Sci* 1995, 55, 107.
- Halasz, L.; Vorster, O. C.; Pizzi, A.; Guasi, K. In *Proceedings of the 14th PAC Symposium, Warsaw, Poland, July 2000*.
- Halasz, L.; Vorster, O. C.; Pizzi, A.; van Alphen, J. *J Appl Polym Sci* 2000, 75, 1296.
- Halasz, L.; Vorster, O. C.; Pizzi, A.; Guasi, K. *J Appl Polym Sci* 2001, 80, 898.
- Pizzi, A.; Lu, X.; Garcia, R. *J Appl Polym Sci* 1999, 71, 915.
- Pizzi, A.; Zhao, C.; Kamoun, C.; Heinrich, H. *J Appl Polym Sci* 1999, 80, 2128.
- Fevre, A.; Murat, M. *J Thermal Anal* 1975, 7, 429.
- Carter, R. E. *J Chem Phys* 1961, 34, 2010.
- Enns, J. B.; Gillham, J. K. *J Appl Polym Sci* 1983, 28, 2831.
- Nunez, L.; Fraga, F.; Nunez, M. R.; Villanueva, M. *J Appl Polym Sci* 1998, 70, 1931.