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Study of network formation in furfuryl methacrylate photopolymerisation at different temperatures. The Tobita method applied to the polymerisation at low conversions[☆]

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Abstract

The kinetics modelling of furfuryl methacrylate photopolymerisation using the method of moments has enabled to obtain the concentrations of radicals and pendant groups in the networks formed at different temperatures. The analysis of these results has shown which simple step of the polymerisation mechanism is favoured according to the reaction temperature. For example, at a temperature of 283 K, intermolecular degradative transfer to the furan ring plays an important role in network formation. On the other hand, some results obtained by kinetics modelling were used to evaluate the crosslink density of the network. With this aim, the Tobita pseudo-kinetics constants method was applied to the polymerisation at low conversions. The values of crosslink density obtained by means of kinetics modelling and the Tobita method were in good agreement. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Tobita method; Photopolymerisation; Kinetics modelling

1. Introduction

For the past few years, one of the most attractive topics in the field of theoretical polymer science has been that of the formation of networks by radical polymerisation and polycondensation [1–15]. In certain works, different mathematical approaches have been used to theoretically describe the structure and properties of gels formed during polymerisation, namely, the Monte Carlo[2] method, cascade theory [3,5], the stoichiometric method [8], and the method of moments. On the other hand, the phenomenon of network formation in the radical photopolymerisation of acrylic-furan compounds, and, in particular, the case of furfuryl methacrylate (see Fig. 1), has recently been studied by modelling [16,17]. The theoretical efforts made to gain insight into the polymerisation mechanism of this monomer are due to its potential use in the preparation of photopolymerisable biomaterials at low temperatures [18–20]. Thus, when the monomer is copolymerised with other compounds that have a hydrophilic character, semipermeable biocompatible gels can be obtained. For example, these hydrogels have shown to be useful as vehicles for the delivery of pharmaceuticals. In such applications, the drug diffusion through the gel often determines the performance of the resulting product. The permeability or diffusion of the drug, as well as the degree of swelling, depend notably on pendant group concentrations, crosslink density, and mean length or molecular weight of chains between croslinks when the network is used as a matrix [21,22].

Often, in the case of complex polymerising systems in which insoluble gels are obtained, the values of the parameters that characterise network structure (for example crosslink density and pendant group concentrations) are not easily obtained experimentally. However, they can readily be estimated by theoretical methods, for instance, by means of kinetics modelling using the method of moments [11,17,23]. These mathematical tools enable the different moments of the molecular weight distribution to be calculated, and all the above-mentioned parameters to be obtained from them. On the other hand, the analysis of the behaviour of these parameters as functions of the polymerisation temperature can produce a reasonably clear picture about the development of the formation of the network.

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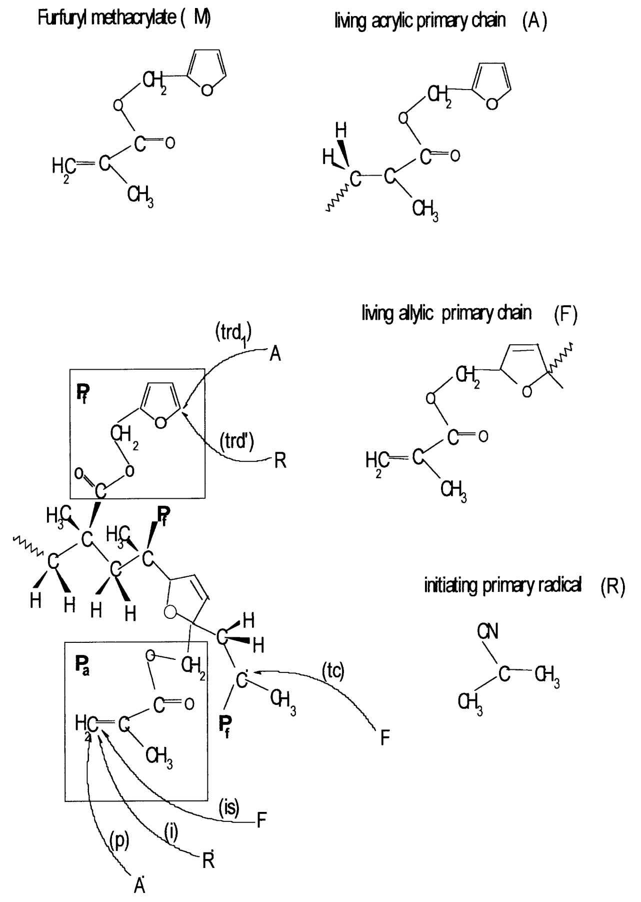

Fig. 1. Reactions involved in the furfuryl methacrylate crosslinking polymerisation.

Thus, with this goal in mind, modelling the influence of the polymerisation temperature on those parameters characterising network structure (primary chain length distribution, moments of the network molecular weight distribution and related parameters) was first studied. Secondly, Tobita's pseudo-kinetics constant method was extended to describe the average crosslink density of the network, and to corroborate results obtained by kinetics modelling. In turn, the development of the Tobita method for this particular type of polymerisation provides a simple tool for estimating crosslink density in the gels obtained.

2. Theoretical section

2.1. Kinetics mechanism involved in network formation for furfuryl methacrylate polymerisations

The photopolymerisation mechanism of furfuryl methacrylate (symbolised with M in Fig. 1) consists mainly of five simple steps: initiation (i), propagation (p), degradative transfers (include primary (′trd) and intermolecular (trd_1)), re-initiation (is) and crosstermination (tc) [16,17]. These processes take place in crosslinking and reactions between the different types of pendant groups and radicals on the polymeric chains. Thus, for example, propagation, initiation, and re-initiation result in the consumption of pendant acrylic groups (P_a) and the conversion of crosslinked units (P_f) into the polymeric network. In addition to this, in the specific case of initiation, acrylic type radicals (A) are formed, and initiating primary radicals (R) disappear from the system. On the other hand, when a reaction occurs at the C-5 position of the furan ring and either an A or a R radical, a degradative transfer takes place with the formation of allylic type radicals (F) [24]. In this process, as F is stabilised and sterically hindered; both the rate and molecular weight obtained are expected to decrease (auto-retardation phenomenom) [25,26]. Of two possible degradative transfer processes, the intermolecular degradative transfer process has been demonstrated by modelling to be the most important reaction in the crosslinking process [17]. This reaction produces P_a and causes the disappearance of A in the network as well as the inclusion of dihydrofuran units in the polymeric backbone. A completely different picture to intermolecular degradative transfer is the re-initiation that creates A from F, and leads to the formation of pendant furan groups (P_f) on the polymer chains. These groups are also produced during the propagation process without either the consumption or production of A. Only in the case of crosstermination, A and F are consumed simultaneously without altering the amount of non-crosslinked pendant groups in the network. Sensitivity analysis has confirmed that, of the all termination steps [17], crosstermination is the only one to occur. Taking into account this kinetics scheme, the method of moments for modelling the crosslinked photopolymerisation of furfuryl methacrylate has been developed.

2.2. Method of moments for crosslinked polymerisation of furfuryl methacrylate

The structure of a network formed during polymerisation can be described by means of different molecular weight averages of the primary chains that would result if all crosslinks were severed. Averages, such as number-average chain length (NACL) and weight-average chain lenght (WACL), as well as the composition of pendant groups, are calculated by the method of moments [23]. This method was developed for the case of furfuryl methacrylate photopolymerisation, taking into account the preceding kinetics scheme, and is described elsewhere [17] in more detail. According to this scheme, three types of species: $A_{a,f,r}$, $F_{a,f,r}$, $P_{a,f,r}$ can be formed throughout the polymerisation. The first two species are acrylic and allylic living primary chains, respectively, whereas the latter one is dead. Three subscripts to describe the composition of primary chains in the network were used [17]. These correspond to the number of pendant acrylic groups (a), furan groups (f) and crosslinks (r) per chain. The rate expressions for the formation of each species obtained according to the material balance in the kinetics scheme are:

$$\begin{aligned}\frac{\mathrm{d}[A_{a,f,r}]}{\mathrm{d}t} &= \{\delta(a,f-1,r)k_i[R] + k_p([A_{a,f-1,r}]) \\ &\quad + k_{is}[F_{a,f-1,r}]\}[M] + \{\delta(a,f,r-1)k_i[R] \\ &\quad + k_p[A_{a,f,r-1}] + k_{is}[F_{a,f,r-1}]\}[P_a] - \{k_i[R] \\ &\quad + k_{is}[F] + k_p[A]\}\{a[A_{a,f,r}] - (a+1) \\ &\quad \times [A_{a+1,f,r-1}]\} - \{k'_{\mathrm{trd}}[R] + k_{\mathrm{trd1}}[A]\}\{f[A_{a,f,r}] \\ &\quad - (f+1)[A_{a,f+1,r-1}]\} - \{(k_p[P_a] + k_{\mathrm{trd1}}[P_f]) \\ &\quad + k_{tc}[F]\}[A_{a,f,r}]\end{aligned} \tag{1}$$

$$\begin{aligned}\frac{\mathrm{d}[F_{a,f,r}]}{\mathrm{d}t} &= \{k_{\mathrm{trd1}}[A_{a-1,f,r}] + \delta(a-1,f,r)k'_{\mathrm{trd}}[R]\}[M] \\ &\quad + \{k_{\mathrm{trd1}}[A_{a,f,r-1}] + \delta(a,f,r-1)k'_{\mathrm{trd}}[R]\}[P_f] \\ &\quad - \{k_i[R] + k_{is}[F] + k_p[A]\}\{a[F_{a,f,r}] - (a+1) \\ &\quad \times [F_{a+1,f,r-1}]\} - \{k'_{\mathrm{trd}}[R] + k_{\mathrm{trd1}}[A]\}\{f[F_{a,f,r}] \\ &\quad - (f+1)[F_{a,f+1,r-1}]\} - \{k_{is}([MF] + [P_a]) \\ &\quad + k_{tc}[A]\}[F_{a,f,r}]\end{aligned} \tag{2}$$

$$\begin{aligned}\frac{\mathrm{d}[P_{a,f,r}]}{\mathrm{d}t} &= -\{k_i[R] + k_{is}[F] + k_p[A]\}\{a[P_{a,f,r}] - (a+1) \\ &\quad \times [P_{a+1,f,r-1}]\} - \{k'_{\mathrm{trd}}[R] + k_{\mathrm{trd1}}[A]\}\{f[P_{a,f,r}] \\ &\quad - (f+1)[P_{a,f+1,r-1}]\} - k_{tc}\sum_{x,y,z=0}^{a,f,r}\left[A_{a-x,f-y,z-r}\right] \\ &\quad \times [F_{x,y,z}]\end{aligned} \tag{3}$$

where δ is Kronecker's delta and is given by

$$\delta(a,f,r) \equiv \delta(a)\delta(f)\delta(r) \qquad \delta(i) \equiv \left[\begin{array}{ll} 1 & \text{for } i = 0 \\ 0 & \text{for } i = 1 \end{array}\right.$$

These expressions enable the rate of chain length distribution moments $r_{\psi_{i,j,k}}$ to be obtained (see Appendix A). From the chemical point of view, the zero order moment $((i,j,k = 0))$ characterises the formation rate of all primary chains in the network, whereas the first order moments describe the rates of formation of pendant acrylic $(i = 1, j = 0, k = 0)$, furan $(i = 0, j = 1, k = 0)$, and crosslinked $(i = 0, j = 0, k = 1)$ groups. Fortunately, as these moments depend only on moments of equal and lower order, the closure method for an infinite set of moment equations [27,28] is not used since it would introduce approximations from a mathematical point of view. However, equations for $r_{\psi_{i,j,k}}$ of combined first (for example $i = 1, j = 0, k = 1$) and higher orders without applying such a method can be developed. (This will be discussed in a forthcoming paper for the case of furfuryl acrylate photopolymerisation).

From numerical integration of the $r_{\psi_{i,j,k}}$, the cumulative number-average chain length (NACL), the cumulative weight-average chain length (WACL), the cumulative number-average degree of branching (NADB), and the cumulative weight-average degree of branching (WADB) of the primary chains can be estimated [29]. The two last averages are very important since physical properties such as intrinsic viscosity and melt viscosity are more sensitive to the structure of the larger molecules in the system. The definitions of NACL ($\bar{X}_{\mathrm{N}}$), WACL ($\bar{X}_{\mathrm{w}}$), NADB ($\bar{B}_{\mathrm{N}}$), and WADB ($\bar{B}_{\mathrm{w}}$), for furfuryl methacrylate polymerisation are given below:

$$\bar{X}_{\mathrm{N}} = \frac{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}}{\psi_{0,0,0}} \tag{4}$$

$$\bar{X}_{\mathrm{w}} = \frac{\psi_{2,0,0} + \psi_{0,2,0} + \psi_{0,0,2} + 2(\psi_{1,1,0} + \psi_{1,0,1} + \psi_{0,1,1})}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} \tag{5}$$

(see Appendix B).

$$\bar{B}_{\mathrm{N}} = \frac{\psi_{0,0,1}}{\psi_{0,0,0}} \tag{6}$$

$$\bar{B}_{\mathrm{w}} \approx \frac{\psi_{1,0,1} + \psi_{0,1,1} + \psi_{0,0,2}}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} \tag{7}$$

Here $\psi_{1,0,0}, \psi_{0,1,0}, \psi_{0,0,1}$ denote, respectively, the acrylic, furan and crosslinked group concentrations into the network, whereas $\psi_{0,0,0}$ is the global concentration of primary chains in the network. Additional definitions of these moments can be found elsewhere [17].

On the other hand, another parameter characterizing the network structure is the crosslink density ($\bar{\rho}$), which can also be obtained from the moments

$$\bar{\rho} = \frac{\psi_{0,0,1}}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} = \frac{\bar{B}_{\mathrm{N}}}{\bar{X}_{\mathrm{N}}} \tag{8}$$

All the moments are closely related to the rates of the simple steps involved in network formation. In turn, as these rates depend on the polymerisation temperature, the values of the moments will also be functions of the temperature. As a consequence, a change in temperature results in a change in moment values, according to the activation energies of the processes involved in the network formation. Thus, from the results of the evolution of moment values with conversion and the activation energies of such processes, it is possible to deduce which of the simple steps is the principal contributor to network formation at various reaction temperatures.

3. Tobita's pseudo-kinetics constant method

Another way of modelling the formation of the network is by Tobita's method of pseudo-kinetics constants. Using this kinetics approach for the copolymerisation of a vinyl monomer with a divinyl comonomer [14], two pseudo-kinetics rate constants were obtained, namely crosslinking (K_p^*) and propagation ($\bar{K}_p$), according to the following expressions:

$$K_p^* = \left(k_{13}^*\phi_1^0 + k_{23}^*\phi_2^0 + k_{33}^*\phi_3^0\right)\{\bar{F}_2 - \bar{\rho}_a - \bar{\rho}_c\} \tag{9}$$

$$\bar{K}_p = (k_{11}f_1 + k_{12}f_2)\phi_1^0 + (k_{21}f_1 + k_{22}f_2)\phi_2^0 + (k_{31}f_1 + k_{32}f_2)\phi_3^0 \tag{10}$$

Here k_{ij} is the propagation rate constant in which the radical of type i reacts with the double bond of type j, f_i the mole fraction of monomer type i, ϕ_i^0 the mole fraction of radical type i, k_{i3}^* the rate constant for crosslinking reaction in which radical of type i reacts with the double bond of type j, $\bar{F}_2$ the cumulative mole fraction of divinyl monomer in the chains of the polymer formed and $\bar{\rho}_a$, $\bar{\rho}_c$ are the cumulative fractions of crosslinked units and cycles, respectively, in the polymer.

These pseudo-kinetics rate constants can be modified for the case of polymerisation of acryl-furan compounds if they are supposed to form as crosslinked internal copolymerisations. That is, the acrylic and furan groups in a molecule of M (Fig. 1) are considered as independent comonomers in the polymerisation [17]. Therefore, four types of radical reactions are possible for this system: (1) acrylic radical with acrylic double bond ($k_{11} = k_p$), (2) acrylic radical with furan double bond ($k_{12} = k_{\mathrm{trd1}}$), (3) allylic radical with acrylic group ($k_{21} = k_{is}$), and (4) allylic radical with furan double bond ($k_{22} = k_{\mathrm{pff}}$). Bearing in mind the assumed scheme, by analogy with vinyl/divinyl copolymerisation systems, the propagation and crosslinking pseudo-kinetics rate constants for this type of polymerisation are defined as follows:

$$\bar{k}_p = (k_p f_1 + k_{\mathrm{trd1}} f_2)\phi_1^0 + (k_{is} f_1)\phi_2^0 \tag{11}$$

$$k_p^* = k_{\mathrm{trd1}}\phi_1^0 \frac{\psi_{0,1,0}}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} + \left(k_p\phi_1^0 + k_{is}\phi_2^0\right)\frac{\psi_{1,0,0}}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} \tag{12}$$

where

$$\phi_1^0 = \frac{[A]}{[A] + [F]} \tag{13}$$

$$\phi_2^0 = \frac{[F]}{[A] + [F]} \tag{14}$$

$$f_1 = 1/2 + \frac{\psi_{1,0,0}}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} \tag{15}$$

$$f_2 = 1/2 + \frac{\psi_{0,1,0}}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}} \tag{16}$$

are mole fractions of acrylic and allylic radicals, and acrylic and furan groups in the feed, respectively.

The following simplifying assumptions were made:

1. Cyclisation reaction does occur in bulk ($\bar{\rho}_c = 0$).
2. Reactivities of double bonds in the monomer do not change when some of them have reacted. Therefore, the kinetics rate constants are assumed to be the same for reactions between monomers and radicals and polymer and radicals (crosslinking reactions).
3. Reaction between F radicals and the furan ring ($k_{22} = 0$) is negligible because F radicals are stable, or because of steric hindrance.

Since the values of pseudo-kinetics constants can be obtained, it is possible to determine the average crosslink density in the polymeric network at conversion x, by means of the following equation:

$$\bar{\rho}(x) = \frac{k_p^*}{\bar{k}_p x}\left\{\ln\left[\frac{1}{1-x}\right] - x\right\} \tag{17}$$

In this way, knowing the change of ($k_p^*/\bar{k}_p$) with conversion and polymerisation temperature, it is possible to estimate how favoured are the cross-linking steps compared to propagation for this type of system.

4. Analysis of results

4.1. *Influence of polymerisation temperature on the concentration of pendant groups and radicals in the network*

Modelling of the experimental kinetics curve at different polymerisation temperatures has enabled the first order moments of the distribution of primary chain lengths in the networks to be obtained ($\psi_{1,0,0}$, $\psi_{0,1,0}$, $\psi_{0,0,1}$) [17]. The evolutions of these moments (concentrations of pendant groups in the network) with conversion at polymerisation temperatures of 273, 283, 303 and 313 K, are shown in Figs. 2–4. Further, the concentrations of acrylic $[A]$ and allylic $[F]$ radicals involved in the formation of the network are shown in Figs. 5 and 6.

From the results shown in these figures (taking Fig. 4 as an example), one might conclude that the concentration of crosslinking in the network ($\psi_{0,0,1}$) is practically unaffected by temperature. However, Figs. 2 and 3 show that temperature has an influence on the structure of the networks, since

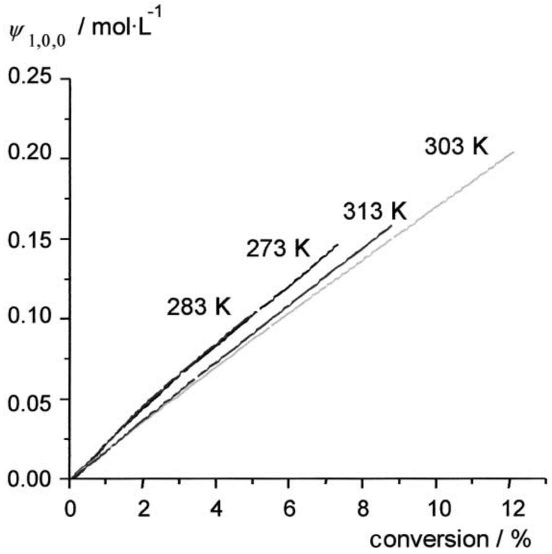

Fig. 2. Evolution of pendant acrylic group concentration ($\psi_{1,0,0}$) with conversion at different polymerisation temperatures (T).

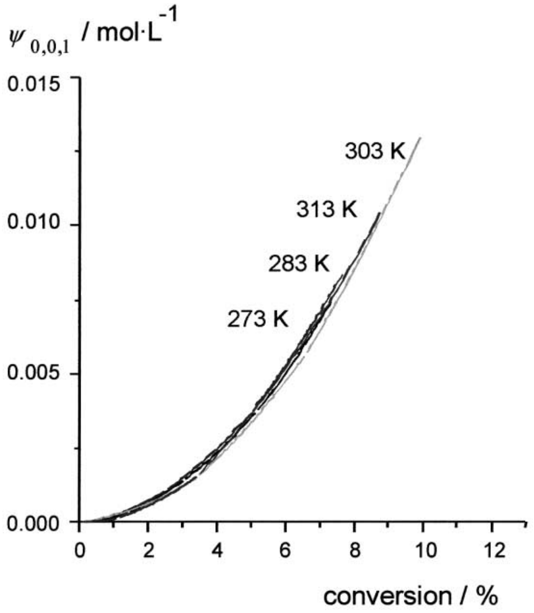

Fig. 4. Evolution of crosslinked group concentration ($\psi_{0,0,1}$) with conversion at different polymerisation temperatures (T).

certain changes in the concentration of the pendant acrylic and furanic groups ($\psi_{1,0,0}$, $\psi_{0,1,0}$) are noticeable over the temperature range 273–303 K. These results indicate that the polymerisation temperature influences, in different ways, the velocity of each simple step in the kinetics mechanism of the network formation. This is due to the differences in activation energy between each of the steps (Table 1). These mean that as the polymerisation temperature increases so also should the relative velocities of those steps of greater activation energy. Hence, in the case of this particular system, when the temperature is increased from 273 to 283 K, a diminution in the concentration of acrylic radicals [A] is observed, as well as an increase in the concentration of allyl radicals [F] (to a maximum). This seems to indicate that at 283 K the intermolecular degradative transfer step (IDTP) is strongly favoured in comparison to the other steps.

On the other hand, from an inspection of the values of activation energies shown in Table 1, one might conclude that propagation is a step that competes against degradative transfer, due to the similar values of their activation energies. At a temperature of 303 K, propagation is favoured over IDTP, as seen in Figs. 2 and 3. This conclusion is also in agreement with the values of number-average length of the primary chains in the networks (NACL) at different temperatures, as in Fig. 7 it can be seen that as the temperature rises from 283 to 303 K, the value of NACL

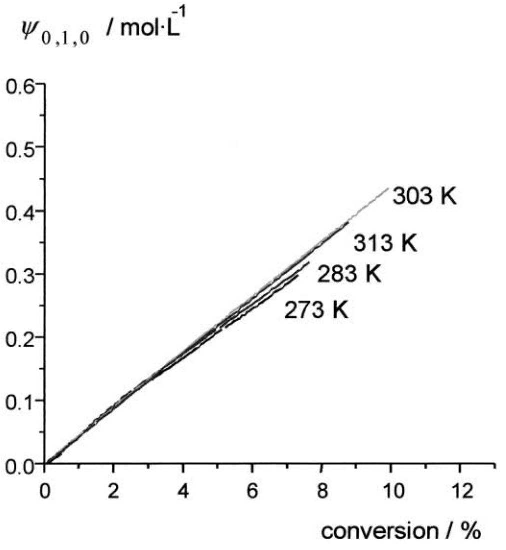

Fig. 3. Evolution of pendant furan group concentration ($\psi_{0,1,0}$) with conversion at different polymerisation temperatures (T).

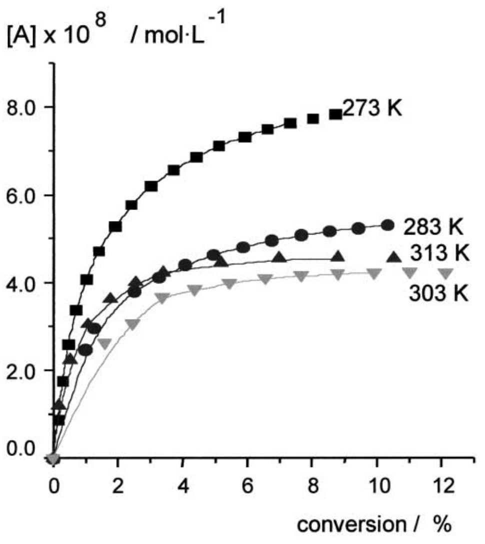

Fig. 5. Evolution of acrylic radical concentration ([A]) with conversion at different polymerisation temperatures (T).

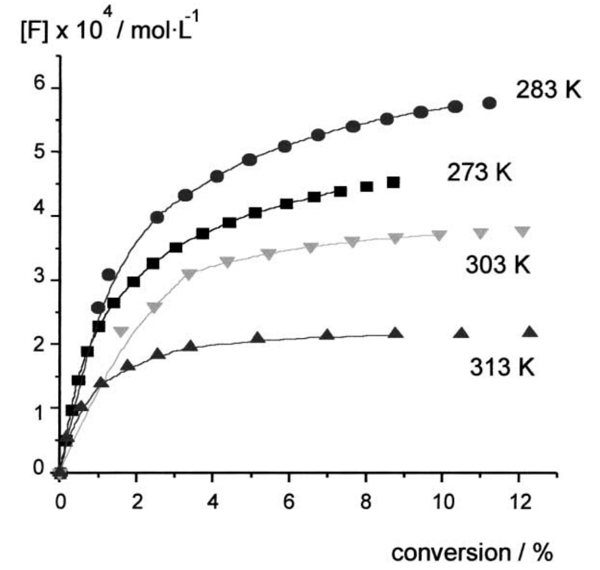

Fig. 6. Evolution of allylic radical concentration ($[F]$) with conversion at different polymerisation temperatures (T).

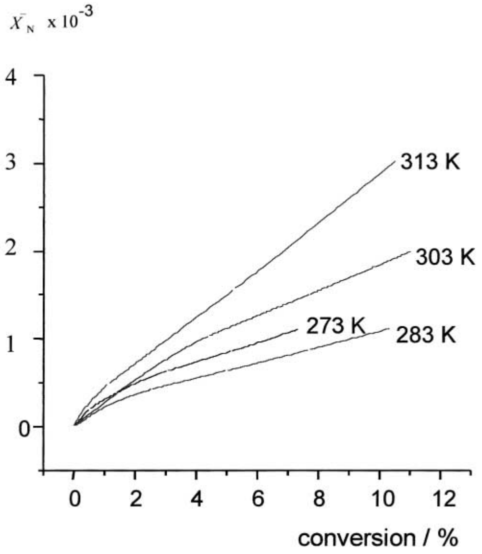

Fig. 7. Evolution of number-average chain length ($\bar{X}_N$) with conversion at different polymerisation temperatures (T).

increases, thereby indicating an increase in the size of the primary chains in the network. From a kinetics point of view, this phenomenon results from the process of degradative transfer being less favoured than that of propagation.

Also, from Figs. 5 and 6 it can be seen how the values of $[F]$ at 313 K are at a minimum, while $[A]$ increases as the temperature is raised from 303 to 313 K. This behaviour shows there is a tendency to favour radical re-initiation at 313 K. On account of this, there tends to be a high concentration of acrylic radicals in the networks at 313 K, hence, a high polymerisation rate, and, as a consequence, a high value of NACL (see Fig. 7).

5. Tobita's method applied to the polymerisation of furfuryl methacrylate

Tobita's method was applied to the case of the polymerisation being studied, and the results obtained for the average crosslink density ($\bar{\rho}$) of the polymeric network with conversion at different temperatures are shown in Figs. 8–10. In these figures, the average crosslink densities computed by kinetics modelling (Eq. (8)) are also presented. For the calculation of the pseudo-kinetics constants by Tobita's method, the rate constants collected in Table 1, the concentrations of non-crosslinked pendant groups ($\psi_{0,1,0}, \psi_{1,0,0}$) and the radicals concentrations ($[A], [F]$) in the network (Figs. 2, 3, 5 and 6) were used. From Figs. 8–10, it can be seen that the results obtained from the kinetics modelling and Tobita's method are in a good agreement. Statistically, both methods show no significant difference in their predictions of the crosslink density (see Table 2), in spite of the difference that was found between them at 273 K (about 15%). This difference is plotted in the figures using bars.

The values of $\bar{\rho}$ estimated by both methods are found to be about 10^{-2} for different polymerisation temperatures. The values are not so different from those obtained for other crosslinked systems. For example: methyl methacrylate/ethylene di-methacrylate and styrene/divinyl benzene

Table 1

Rate constants (in l mol^{-1} s^{-1}) at different temperatures T (in K) for different processes involved in the crosslinked photopolymerisation of furfuryl methacrylate. In the last column, the activation energies (in kcal mol^{-1}) for these processes are collected. All these values were extracted from elsewhere [16,17]

Radicalic process (rate constant symbol)	T				Activation energy
	273	283	303	313	
Primary initiation (k_{in})	20	28.93	38.86	44.02	0.9
Intermolecular degradative transfer (k_{trd1})	560	1035	1384	2095	4.2
Propagation (k_p)	560	1035	2094	2878	4.8
Crosstermination (k_{tc})	1.008×10^{-4}	1.666×10^{-4}	3.122×10^{-4}	9.13×10^{-4}	8.54
Primary degradative transfer (k'_{trd})	564.2	1781	5456	8970	9.3
Re-initiation (k_{is})	0.1	0.14	0.252	0.7398	11.1

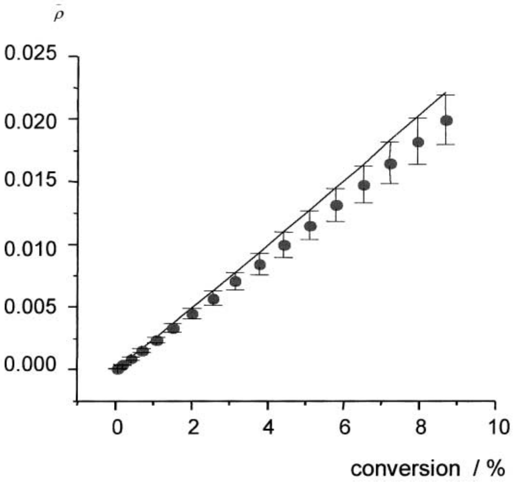

Fig. 8. Evolution of crosslink density of the network ($\bar{\rho}$) with conversion at polymerisation temperature $T = 273$ K. The points plotted were obtained by kinetics modelling while the lines were obtained by means of Tobita's method.

$\bar{\rho} \sim 10^{-3}$. The difference of an order of magnitude is not surprising because the crosslink density depends on the amount of crosslinking agent used in the polymerisation. Thus, as in the copolymerisation of vinyl/divinyl systems, the initial concentration of divinyl comonomer used in relation to the vinyl monomer was low ($f_{20} = 0.01$ was the initial mole fraction of divinyl comonomer in the feed), the amount of pendant double bonds incorporated in the polymer was also low, resulting in a low average crosslink density in the network. In the case of the polymerisation of furfuryl methacrylate, it has been proved that the crosslinking occurs mostly through IDTP between acrylic radicals and pendant furan rings on the polymer [17]. Futhermore, as furan rings are at high concentrations in the polymeric chains (up to 0.6 mol l^{-1}, $f_{20} = 0.5$), a network with higher crosslink density would be expected.

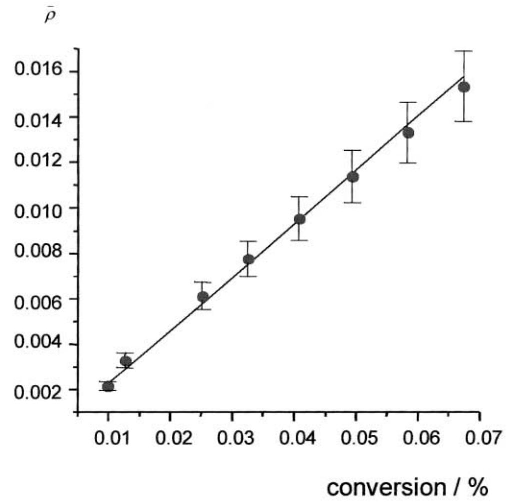

Fig. 9. Evolution of crosslink density of the network ($\bar{\rho}$) with conversion at polymerisation temperature $T = 283$ K. The points plotted were obtained by kinetics modelling while the lines were obtained by means of Tobita's method.

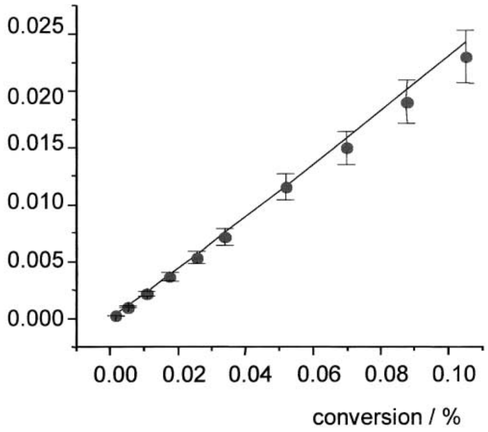

Fig. 10. Evolution of crosslink density of the network ($\bar{\rho}$) with conversion at polymerisation temperature $T = 303$ K. The points plotted were obtained by kinetics modelling while the lines were obtained by means of the Tobita's method.

6. Conclusions

A means has been developed, based on the method of moments, for modelling the polymerisation kinetics of acrylfuranic compounds. The equations that describe these methods (Appendices A and B) allow the structural parameters of networks formed, such as $\bar{X}_\mathrm{N}$, $\bar{X}_\mathrm{w}$, $\bar{B}_\mathrm{N}$, $\bar{B}_\mathrm{w}$, and $\bar{\rho}$, to be determined. From first order moments of the distributions of primary chain lengths in the networks, and from the concentrations of species polymerising, it was possible to elucidate the dominant step in the polymerisation mechanism, at different temperatures of polymerisation. For example, at temperatures of 273–283 K, IDTP is the dominant step, while at higher temperatures the propagation and re-initiation steps are more significant.

Tobita's method of pseudo-kinetics constants was developed to predict the crosslink densities of acrylfuranic polymers. The results show that Tobita's method and that of modelling are statistically equivalent. The practical

Table 2
Goodness-of-fit test using χ^2. The χ^2 values were computed using as observed frequencies (O_i) the values of crosslink density obtained from Tobita's model, and as expected ones (E_i) those obtained from mathematical modelling. When $\chi^2_\mathrm{exp} < \chi^2_\mathrm{theo}$, there is no significant difference between the two methods

T (K)	χ^2_exp [a]	χ^2_theo	Df
273	1.539×10^{-3}	26.3	16
283	1.046×10^{-4}	14.07	7
303	3.423×10^{-4}	16.92	9

[a] $\chi^2_\mathrm{exp} = \sum_{i=1}^{n} (O_i - E_i)/E_i$, n: number of points on the curve χ^2_theo is extracted from a table of percentage points of the χ^2 distribution for df degrees of freedom (df $= n - 1$) and a 95% level of significance.

importance of this result is that, knowing the values of the pseudo-kinetics constants, it is possible to predict simply the density of crosslinks by the method of Tobita, without becoming involved in solving complicated non-lineary ordinary differential equations.

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Appendix A. Formulation of the moment equations

Let

$$\psi_{i,j,k} = \sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty} a^i f^j r^k([A_{a,f,r}] + [F_{a,f,r}] + [P_{a,f,r}])$$

and

$$r_{\psi_{i,j,k}} = r_{\lambda^A_{i,j,k}} + r_{\lambda^F_{i,j,k}} + r_{\lambda^P_{i,j,k}}$$

then

$$r_{\lambda^A_{i,j,k}} = \sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty} a^i f^j r^k \frac{\mathrm{d}[A_{a,f,r}]}{\mathrm{d}t}$$

From Eq. (1) in text we can obtain $r_{\lambda^A_{i,j,k}}$ which is given by

$$\begin{aligned}
r_{\lambda^A_{i,j,k}} = {} & \left\{\delta(i,k)k_i[R] + k_p\sum_b^j \binom{j}{b}\lambda^A_{i,b,k} + k_{is}\sum_b^j \binom{j}{b}\lambda^F_{i,b,k}\right\} \\
& \times[M] + \Bigg\{\{\delta(i,j)k_i[R] + k_p\sum_c^k \binom{k}{c}\lambda^A_{i,j,c} \\
& + k_{is}\sum_c^k \binom{k}{c}\lambda^F_{i,j,c}\Bigg\}[P_a] - \{k_i[R] + k_{is}[F] \\
& + k_p[A]\}\Bigg\{\lambda^A_{i+1,j,k} - \Bigg(\sum_a^{i+1}\sum_c^k \binom{k}{c}\binom{i+1}{a} \\
& \times(-1)^{i+1-a}\lambda^A_{a,j,c} + \sum_a^i\sum_c^k \binom{k}{c}\binom{i}{a}(-1)^{i-a}\lambda^A_{a,j,c}\Bigg)\Bigg\} \\
& - \{k'_{\text{trd}}{*}[R] + k_{\text{trd1}}[A]\}\Bigg\{\lambda^A_{i,j+1,k} - \Bigg(\sum_b^{j+1}\sum_c^k \binom{k}{c} \\
& \times\binom{j+1}{b}(-1)^{j+1-b}\lambda^A_{i,b,c} + \sum_b^j\sum_c^k \binom{k}{c}\binom{j}{b} \\
& \times(-1)^{j-b}\lambda^A_{i,b,c}\Bigg)\Bigg\} - \{(k_p + k_{\text{trd1}})[M] + k_p[P_a] \\
& + k_{\text{trd1}}[P_f] + k_{tc}[F]\}\lambda^A_{i,j,k}
\end{aligned}$$

Here, for instance, it can be proved that in terms of moments

$$\begin{aligned}
& \sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty} a^i f^j r^k (a+1)([A_{a+1,f,r-1}]) \\
& = \sum_a^{i+1}\sum_c^k \binom{k}{c}\binom{i+1}{a}(-1)^{i+1-a}\lambda^A_{a,j,c} + \sum_a^i\sum_c^k \binom{k}{c} \\
& \times\binom{i}{a}(-1)^{i-a}\lambda^A_{a,j,c}
\end{aligned}$$

and

$$\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty} a^i f^j r^k \delta(a,f-1,r) = \delta(i,k)$$

Equally the moment equations for species F and P were derived and are given by

$$\begin{aligned}
r_{\lambda^F_{i,j,k}} = {} & \left\{k_{\text{trd1}}\sum_a^i \binom{i}{a}\lambda^A_{a,j,k} + \delta(j,k)k'_{\text{trd}}[R]\right\}[M] \\
& + \left\{k_{\text{trd1}}\sum_c^k \binom{k}{c}\lambda^A_{i,j,c} + \delta(j,k)k'_{\text{trd}}[R]\right\}[P_f] - \{k_i[R \\
& + k_{is}[F] + k_p[A]\}x\Bigg\{\lambda^F_{i+1,j,k} - \Bigg(\sum_b^{i+1}\sum_c^k \binom{k}{c} \\
& \times\binom{i+1}{a}(-1)^{i+1-a}\lambda^F_{a,j,c} + \sum_a^i\sum_c^k \binom{k}{c}\binom{i}{a} \\
& \times(-1)^{i-a}\lambda^F_{a,j,c}\Bigg)\Bigg\} - \{k'_{\text{trd}}[R] + k_{\text{trd1}}[A]\}x\Bigg\{\lambda^P_{i,j+1,k} \\
& - \Bigg(\sum_b^{j+1}\sum_c^k \binom{k}{c}\binom{j+1}{b}(-1)^{j+1-b}\lambda^F_{i,b,c} \\
& + \sum_b^j\sum_c^k \binom{k}{c}\binom{j}{b}(-1)^{j-b}\lambda^F_{i,b,c}\Bigg)\Bigg\} - \{k_{is}([M] \\
& + [P_a]) + k_{tc}[A]\}\lambda^F_{i,j,k},
\end{aligned}$$

$$\begin{aligned}
r_{\lambda^P_{i,j,k}} = {} & -\{k_i[R] + k_{is}[F] + k_p[A]\}x\Bigg\{\lambda^P_{i+1,j,k} \\
& - \Bigg(\sum_a^{i+1}\sum_c^k \binom{k}{c}\binom{i+1}{a}(-1)^{j+1-a}\lambda^P_{a,j,c} \\
& + \sum_a^i\sum_c^k \binom{k}{c}\binom{i}{a}(-1)^{i-a}\lambda^P_{a,j,c}\Bigg)\Bigg\} - \Bigg\{k'_{\text{trd}}[R] \\
& + k_{\text{trd1}}[A]\}x\{\lambda^P_{i,j+1,k} - \Bigg(\sum_b^{j+1}\sum_c^k \binom{k}{c}\binom{j+1}{b} \\
& \times(-1)^{j+1-b}\lambda^P_{i,b,c} + \sum_b^j\sum_c^k \binom{k}{c}\binom{j}{b}(-1)^{j-b}\lambda^P_{i,b,c}\Bigg)\Bigg\} \\
& + k_{tc}\sum_a^i\sum_b^j\sum_c^k \binom{i}{a}\binom{k}{c}\binom{j}{b}\lambda^A_{a,b,c}\lambda^F_{i-a,j-b,k-c}
\end{aligned}$$

where

$$[P_a] = \chi_{1,0,0}; \qquad [P_f] = \chi_{0,1,0}; \qquad [P_r] = \frac{1}{2}\chi_{0,0,1}$$

By means of these equations the zero and first order moments could be obtained as described in Ref. [17], Eqs. (9)–(12) for $\mu = 1$.

The moment rate equations can also be obtained through the discrete transformation of total primary molecule number distribution present in the network ($T_{a,f,r} = [A_{a,f,r}] + [F_{a,f,r}] + [P_{a,f,r}]$). Defining a transformation of this distribution by means of the following equation:

$$\bar{T}(\alpha, \varphi, \rho) = \sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty} \alpha^a \varphi^f \rho^r T_{a,f,r}$$

we have that $r_{\psi_{i,j,k}}$ will be given by

$$r_{\psi_{i,j,k}} = \frac{\partial}{\partial t}\left(\frac{\partial^{i+j+K}\bar{T}(\alpha, \varphi, \rho)}{\partial(\log \alpha)^i \, \partial(\log \varphi)^j \, \partial(\log \rho)^k} \right)\Bigg|_{\alpha,\varphi,\rho=1}$$

where, for example

$$\psi_{0,0,0} = \bar{T}(1,1,1); \qquad \psi_{1,0,0} = \frac{\partial \bar{T}}{\partial \log \alpha}\Big|_{\alpha,\varphi,\rho=1};$$

$$\psi_{0,1,0} = \frac{\partial \bar{T}}{\partial \log \varphi}\Big|_{\alpha,\varphi,\rho=1}; \qquad \psi_{0,0,1} = \frac{\partial \bar{T}}{\partial \log \rho}\Big|_{\alpha,\varphi,\rho=1}$$

Appendix B. Formulation of weight-average length of the primary chains in the network ($\bar{X}_{\mathrm{w}}$)

Let w_1 and w_2 be the molecular weights of the acrylic and allyic units, respectively, and r_1, r_2 be the amounts of these crosslinked units in the polymer. Defining $\bar{X}_{\mathrm{w}}$ by means of the following equation:

$$\bar{X}_{\mathrm{w}} = \frac{\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty}[aw_1 + fw_2 + r_1w_1 + r_2w_2)][a_1 + f + r]T_{a,f,r}}{\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty}[aw_1 + fw_2 + r_1w_1 + r_2w_2)]T_{a,f,r}}$$

and taking into account that $r = r_1 + r_2$, we can get the following approximation for $\bar{X}_{\mathrm{w}}$:

$$\bar{X}_{\mathrm{w}} \cong \frac{\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty}[a + f + r]^2 T_{a,f,r}}{\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty}[a + f + r]T_{a,f,r}}$$

From $[a + f + r]^2 = a^2 + f^2 + r^2 + 2(af + ar + fr)$ we have:

$$\bar{X}_{\mathrm{w}} \cong \frac{\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty}[a^2 + f^2 + r^2 + 2(af + ar + fr)] \times T_{a,f,r}}{\sum_{a=0}^{\infty}\sum_{f=0}^{\infty}\sum_{r=0}^{\infty}[a + f + r]T_{a,f,r}}$$

As $T_{a,f,r} = A_{a,f,r} + F_{a,f,r} + P_{a,f,r}$, from the moment definitions given in the text, we obtain:

$$\bar{X}_{\mathrm{w}} \cong \frac{\psi_{2,0,0} + \psi_{0,2,0} + \psi_{0,0,2} + 2(\psi_{1,1,0} + \psi_{1,0,1} + \psi_{0,1,1})}{\psi_{1,0,0} + \psi_{0,1,0} + \frac{1}{2}\psi_{0,0,1}}$$

Eq. (5) in text.

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