

Modeling of Acrylamide/*N,N'*-Methylenebisacrylamide Solution Copolymerization

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Abstract –

A model of free-radical crosslinking copolymerization in solution, based on Flory's gelation theory and developed by Tobita and Hamielec [Macromolecules, 1989, 22, 3098-3105] has been applied to the system acrylamide/ *N,N'*-Methylenebisacrylamide. The evaluation of missing rate constants was performed by comparing model predictions with experimental measurements of swelling ratios and literature data. This way, the interplay of crosslinking and intramolecular cyclization reactions, regulating the network formation and its properties, has been deepened. It turns out that the primary intramolecular cyclization is practically independent of the crosslinker amount employed, but is affected by the total monomer concentration. For the latter dependency, an empirical correlation was proposed, which was tested in parametric simulations showing its impact on the hydrogels properties.

1 Introduction

Acrylamide (Am)/ *N,N'*-Methylenebisacrylamide (BAm) hydrogels are of paramount importance in a great variety of applications, ranging from superabsorbent materials, electrophoresis gels, supports for cell culture and artificial muscles.¹⁻⁴ In several of the aforementioned applications, the hydrogel structure and molecular weights need to be tailor-made and well-controlled in order to meet the required specification. Mathematical models can be very helpful to design the reaction conditions in optimal way: as a matter of fact, a great deal of modeling tools to predict the properties of such complex nonlinear polymers have been introduced in the past years. The various modelling techniques have to take into account crosslinking and intramolecular reactions, due to the divinyl nature of the BAm. The interplay of these reactions is of utmost importance, as it regulates the material properties in terms of mechanical and swelling response, as well as the onset of the gel formation, after which the polymerization occurs in two phases, named sol and gel. While the sol contains soluble linear and branched chains, the gel phase contains insoluble, highly crosslinked chains, with a virtually infinite molecular weight.

Different modelling approaches have been reported in the literature for crosslinking copolymerization reactions, ranging from deterministic to stochastic and probabilistic ones. As a detailed description of the available crosslinking models is out of the scope of this paper, the different approaches will be only briefly sketched. Kinetic models usually rely on the solution of population balance equations (PBE), which describe among other properties, the chain length distribution (CLD) of the polymer and the crosslinking density. In crosslinking copolymerization, multidimensional PBE are typically needed, as at least the numbers of units and pendant double bonds have to be employed as internal coordinates⁵⁻⁷. Despite the great deal of

information these models provide, their numerical solution, especially when the entire chain length distribution is needed, requires a significant computational effort.

Stochastic Monte Carlo (MC) simulations based on the resolution of chemical master equations have also become popular in the last decades. MC strategies are a versatile tool that can handle complicated problems, as gelation phenomena, and still provide detailed structure of the gel polymer⁸⁻¹². Unfortunately, stochastic methods, despite their relative apparent simplicity, require lengthy computing time to reach sufficient accuracy.

The first statistical approaches date back to the early 40's, where Flory¹³ and Stockmayer^{14, 15} developed a theory of gelation, which is based on the concept of primary chains and on the crosslinking density, representing the probability for a monomer unit to form a link between two chains. The classical Flory-Stockmayer theory¹³⁻¹⁷ has been extended to free-radical crosslinking copolymerization by Tobita and Hamielec who provided a powerful model able to account for different types of intramolecular reactions, such as loop formation, primary and secondary cyclization. In other words, beside average properties, such as sol and gel fractions and sol average molecular weights, also effective and ineffective crosslinking densities can be estimated through this model.

All the aforementioned models require reliable values of the corresponding kinetic parameters for obtaining robust predictions. In the specific case of Am/BAm hydrogels, kinetic parameters concerning propagation and termination have been abundantly discussed in the literature¹⁸. On the other hand, only few papers can be found dealing with the estimation of intramolecular and crosslinking kinetic constants, despite their great importance. Tobita and Hamielec¹⁹ found that with an overall weight fraction of monomer-crosslinker mixture (w_t) of 5.6% (w/w), about 80% of the pendant double bonds (PBD) are consumed by primary cyclization

reactions; and this happens for crosslinker over total monomer mixture weight fraction (w_c) ranging from very large to fairly low values, i.e. from 28% down to 0.02%. A similar amount of PDB consumed by primary cyclization was found by Naghash and Okay²⁰ when performing experiments at $w_t = 1.8\%$ with crosslinker weight fractions in the range $w_c = 5 - 22\%$. On the other hand, Okay et al.²¹ estimate the amount of PDB consumed by primary cyclization as large as 95%, performing experiments at $w_t = 5\%$ with crosslinker contents varying between $w_c = 2 - 15\%$. The discrepancy between these values could be attributed to the experimental techniques employed to determine the PDB conversion: in the cases of Tobita and Hamielec¹⁹ and the first evaluation of Naghash and Okay²⁰, a titration was performed on the sol polymer, whereas swelling measurements of the obtained gel were used to calculate the amount of PDB consumed by cyclizations in the subsequent paper by Okay et al.²¹ Moreover, the crosslinking kinetics has been quantified by Tobita and Hamielec only roughly, as explicitly stated by themselves. It turned out that secondary cyclization is 1000 times more effective than crosslinking in consuming PDB and that the combination of crosslinking and secondary cyclization is a factor 2-4 larger than the propagation kinetic constant.¹⁹

Given the aforementioned discrepancy on the primary cyclization and its expected dependency on the monomer concentration,²² affecting gel formation onset, mechanical and swelling properties, a further estimate for a broad range of monomer concentrations would be desirable.

In this frame, the aim of this work is to estimate the kinetic parameters describing the intramolecular reactions (primary and secondary cyclizations) as well as of the crosslinking reaction at various crosslinker contents and for several monomer concentrations by comparing model predictions with swelling experimental data. In particular, we employed the probabilistic mod-

el proposed by Tobita and Hamielec,²³ which represents an excellent compromise between prediction accuracy and computational effort, thus making it an effective tool towards parameter evaluation. The model predictions are compared to literature data and our own experimental measurements, i.e. swelling ratios of Am/BAm copolymer hydrogels produced at various crosslinker contents ($w_c = 3-5\%$) and different total monomer concentrations ($w_t = 3-16\%$).

2 Materials and methods

2.1 Chemicals

Acrylamide for electrophoresis, 99% was purchased from Sigma. *N,N'*-Methylenebisacrylamide for electrophoresis, 99% and ammonium persulfate (APS) for molecular biology, 98.0% were purchased from Fluka. *N,N,N',N'*-Tetramethylethane 1,2-diamine (TEMED), 99.5% was purchased from Aldrich. All chemicals were used without any further purification. Throughout the study, either MilliQ water or distilled water stripped with nitrogen was used.

2.2 Preparation of the hydrogels

In a typical preparation, required amounts of Am and BAm were solubilized in water previously deoxygenated by nitrogen stripping for at least 20 minutes. The prepared monomer/water solution was again stripped with nitrogen for 10 to 15 minutes; all experiments were carried out at room temperature (25°C). TEMED was charged as such, whereas APS in solution (10% w/w in water). Reactions at different amounts of crosslinker w_c (3, 4 and 5%

w/w, cf. equation (1)) and at different dilution ratios w_t (from 3 to 16% w/w of monomers, cf. equation (2)) were performed; the employed quantities of monomers and initiator are presented in Table 1. In all cases the polymerization duration was 8 hours, but gelation was usually already observed after several minutes. After the reaction, the hydrogel was immersed in excess water.

$$w_c = \frac{m_{crosslinker}}{m_{crosslinker} + m_{monovinyl}} \quad (1)$$

$$w_t = \frac{m_{crosslinker} + m_{monovinyl}}{m_{crosslinker} + m_{monovinyl} + m_{water}} \quad (2)$$

TABLE 1

2.3 Equilibrium swelling ratio

After complete polymerization and immersion in excess water, samples were taken out and cut in 4 slices (between 0.25 and 1g of swollen polymer each). The slice surfaces were dried and weighted before further immersion in water (ca. 30 mL). The sample was weighted daily and subsequently water was changed until equilibrium swelling was achieved. The equilibrium volume fraction of crosslinked polymer ϕ_p is determined gravimetrically assuming the additivity of volumes through equation (3):

$$\phi_p = \left(1 + \frac{(q-1)d_p}{d_w} \right)^{-1} \quad (3)$$

where q is the swelling ratio defined as $m_{polymer} / m_{polymer}^{dry}$, d_p and d_w are the densities of polymer and water, respectively, and $m_{polymer}^{dry}$ the mass of a dried slice of gel whereas $m_{polymer}$ is the mass of the same slice of gel after equilibrium swelling in water has been reached.

3 Model Summary

The chemical species involved in the model are mono- (M_1) and divinyl- (M_2) monomers, pendant double bonds (PDB) and their respective radical species, as clarified in Table 2. The kinetic scheme employed to describe the Am/BAm copolymerization, is detailed in Table 3, whereas the kinetic constants are presented in Table 4. Their estimation, wherever necessary, will be treated in detail in section 4.

TABLE 2

TABLE 3

TABLE 4

The Tobita and Hamielec model enables the calculation of weight fractions of sol and gel, crosslinking densities and average molecular weight between consecutive crosslinks by using three ordinary differential equations and one partial differential equation. The model is based on the calculation of primary chains, defined as those linear chains one would obtain by severing the crosslinkages between them (cf. to Figure 1) and on the crosslinking density ρ (defined as the fraction of crosslinked units over the total number of incorporated monomers) ¹³.

FIGURE 1

The main model assumptions are: (1) quasi steady state assumption (QSSA) for the radicals, (2) monoradical assumption, (3) equality of the kinetic rate constants for sol and gel, (4) negligible penultimate effects, (5) PDB on primary chains consumed only by intramolecular reactions, (6) pseudo-kinetic constants and (7) equal crosslinking density for chains born at the same conversion. The QSSA is well-known and accepted in polymer science since the early work by Stockmayer²⁴ and it has been proven to be a very reasonable assumption when combined with the monoradical one in the presence of crosslinking.²⁵ Furthermore, the monoradical assumption is in the present case fully justified, being the k_p / k_t ratio lower than 10^{-3} .^{25, 26} Moreover, intramolecular cyclizations are known to be dominant in this system, reducing the amount of PDB available for multiradical formation (which in the present case is mediated by crosslinking only). Also assuming the same reactivity of sol and gel is a typical choice when it comes to crosslinking free-radical polymerization,^{5, 23} whereas assumptions (4)-(6) are typically employed in the present model.^{23, 27} As for the employment of pseudo-kinetic constants (assumption (6)), some literature works report the necessity to employing a chain-length dependent termination in the frame of polymer modification.²⁸ Despite the present kinetic scheme is quite different, it is reasonable to assume that a proper chain length dependent termination mechanism is necessary. Nevertheless, to the authors' knowledge, no such expression validated for Am/BAm is provided in the literature, whereas pseudo-kinetic constants have been already successfully employed when modelling this same system.²⁹ Finally, the relevance of assumption (7) has been studied by Zhu and Hamielec,³⁰ who compared simulations results with and without this assumption. It turned out that these effects are important for very short primary chains (10^2 units), in the presence of unequal reactivity of the two monomers ($k_{p22} / k_{p11} \approx 5-10$). As in the present systems the primary chains are known

to be very long (10^5 units¹⁹) and the reactivity of the two monomers differs by a factor 2 only (Table 4), it is expected that the assumption of equal crosslinking density for chains born at the same conversion is quite reasonable.

The model solution can be conveniently organized into three successive steps: i) calculation of the primary chains CLD, ii) estimation of the total crosslinking density ρ and iii) combination of the primary chains according to the crosslinking density to reconstruct sol and gel fractions as well as the average molecular weight between two consecutive crosslinks. Note that the monomer and PDB balances, as well as the pseudo-kinetic constants and the radical balances are reported in the appendix (equations (37)-(46)).

3.1 Primary Chains CLD

As previously mentioned, primary polymer chains are linear and therefore the number and weight CLDs at conversion θ are derived from equations (4) and (5) valid for linear chains³¹:

$$f_n(n, \theta) = \frac{\alpha(\theta)}{(1 + \alpha(\theta))^n} \left[\frac{\tau(\theta) + 0.5\alpha(\theta)\beta(\theta)(n-1)}{\tau(\theta) + 0.5\beta(\theta)} \right] \quad (4)$$

$$f_w(n, \theta) = \frac{\alpha(\theta)}{(1 + \alpha(\theta))^{n+1}} [\tau(\theta) + 0.5\alpha(\theta)\beta(\theta)(n-1)]n \quad (5)$$

where $\tau = \frac{k_{td}^* R_{tot}}{k_{p1}^* M_1 + k_{p2}^* M_2}$, $\beta = \frac{k_{tc}^* R_{tot}}{k_{p1}^* M_1 + k_{p2}^* M_2}$ and $\alpha = \tau + \beta$.

All symbols are detailed in the section Nomenclature.

3.2 Crosslinking density

The crosslinking density of a polymer network depends on the reaction of a radical of one chain with a PDB of another chain, leading to the formation of one effective crosslinkage.

Several intramolecular reactions, such as primary and secondary cyclizations,²³ consume PDB without the formation of effective crosslinkages and need to be accounted for. To clarify the different nature of primary, secondary cycles and crosslinks, consider Figure 2.

FIGURE 2

Moreover, to correctly describe the kinetics of the crosslinkage formation, two time or conversion coordinates have been used, one corresponding to the chain birth and the other to the actual reaction extent, as already discussed by Tobita and Hamielec.²³

In particular, properties characterising the primary chains during their life are called “instantaneous” and properties evolving after chain termination “additional”. Such properties are function of the two coordinates: in terms of conversion, chain birth conversion, θ , and actual conversion, ψ . As an example, at the actual conversion ψ , the total crosslinking density $\rho(\theta, \psi)$ of a primary chain born at conversion θ is the sum of the instantaneous crosslinking density $\rho_i(\theta)$ and the additional crosslinking density $\rho_a(\theta, \psi)$ accumulated after its “death”.

$$\rho(\theta, \psi) = \rho_i(\theta) + \rho_a(\theta, \psi) \quad (6)$$

It is worth noting that implicitly the same value of ρ is assumed whatever the chain length.

3.2.1 *Instantaneous properties*

Crosslinking density – The propagation with PDB leads to the crosslinking of two previously independent chains increasing thus the crosslinking density. The global rate of the crosslinking reaction is:

$$r_{cross} = k_{p_3}^* R_{tot} D_3 \quad (7)$$

D_3 being the PDB concentration, R_{tot} the total radical concentration and k_{p3}^* the pseudo-kinetic rate constant of crosslinking.

The instantaneous crosslinking density is defined as the ratio between the PDB propagation rate and the total rate of monomer incorporation, as defined in (8).

$$\rho_i(\theta) = \frac{k_{p3}^* D_3 R_{tot}}{(k_{p1}^* M_1 + k_{p2}^* M_2) R_{tot}} \quad (8)$$

Primary cyclization – This intramolecular reaction leads to the formation of primary cycles in the polymer network. Primary cycles are only closed by one crosslink and differ on this point from secondary cycles. The mechanism of cyclization was originally proposed by Jacobson and Stockmayer³² for linear polycondensation systems. Further modifications have been proposed by Tobita²⁹ and Zhu et al.³³ They pointed out the importance of properly estimating the cyclization rate in order to evaluate the gel point with accuracy. Indeed, intramolecular primary cyclization leads to the consumption of PDB without linking two primary chains, thus delaying gel formation. According to Landin and Macosko³⁴ the rate of cyclization is proportional to the rate of incorporation of divinyl monomers. The higher the rate of divinyl addition, the higher the number of PDB in the active chains and therefore, the probability of cyclization. This probability is taken into account by the additional coefficient η_{cp} , in the expression of the rate of primary cyclization:

$$r = \eta_{cp} \frac{dM_2}{dt} = \eta_{cp} k_{p2}^* M_2 R_{tot} \quad (9)$$

and the instantaneous primary cyclization density is given by:

$$\rho_{cp}(\theta) = \eta_{cp} \frac{k_{p2}^* M_2}{k_{p1}^* M_1 + k_{p2}^* M_2} = \eta_{cp} X_2 \quad (10)$$

Notably η_{cp} is influenced by many factors, such as flexibility of the chain, amount of cross-linker, primary chains length, quality of the solvent and absolute concentration. All these dependences should be accounted for in a genuinely predictive model: here, we limit ourselves to a constant, effective value, whose validity is therefore restricted to the specific set of operating conditions under examination.

Secondary cyclization – It is worth noting that this monomolecular reaction is assumed to be bimolecular when considering “primary chains”. Let us consider two primary chains (one active and the other terminated) already linked together. The radical can propagate with any type of monomers including its own PDBs: the proximity between the radical and the PDB makes the probability of secondary cyclization larger than that of the reaction with PDB of other chains. Consequently an adjustable quantity, the so-called secondary cyclization constant α_{cs} , is introduced to enhance the corresponding rate constant. It can be greater than unity; moreover it is a function of length of the chains, distance between consecutive PDB, and accessibility of the double bonds entrapped in the polymer network. Because of the lack of understanding for most of these phenomena, also the value of this quantity is assumed to be constant. Despite its roughness, this zero-order approximation has already been proved to provide satisfactory results.²⁹ The rate of secondary cyclization is expressed by:

$$r_{cs} = \alpha_{cs} k_{p3}^* D_3 R_{tot} \quad (11)$$

and the instantaneous secondary cyclization density is given by:

$$\rho_{cs,i}(\theta) = \alpha_{cs} \rho_i(\theta) \quad (12)$$

3.2.2 Additional properties

Additional crosslinking density – The maximum theoretical fraction of crosslinked units (i.e. the crosslinking density) would be equal to the fraction of incorporated divinyl monomer in the active chains (X_2) if no other reactions, apart from crosslinking, consumed them. Actually, the crosslinking density is lower than this maximum value, as several other reactions consume double bonds: primary cyclization and secondary cyclization. Therefore, a partial differential equation describing the additional crosslinking density evolution with conversion has been proposed by Tobita²⁹ as shown in equation (13):

$$\frac{\partial \rho_a(\theta, \psi)}{\partial \psi} = \frac{k_{p3}^* (X_2(\theta) - \rho_{cs,a}(\theta, \psi) - \rho_{cp}(\theta) - \rho_a(\theta, \psi))}{(k_{p1}^* x_1 + k_{p2}^* x_2)(1 - \psi)} \quad (13)$$

where x_1 and x_2 are the monomer fractions corresponding to M_1 and M_2 . In the frame of the zero-order approximation described above, $\rho_{cs,a}$, the additional secondary cyclization, is assumed to be equal to the additional crosslinking density multiplied by α_{cs} :

$$\rho_{cs,a}(\theta, \psi) = \alpha_{cs} \rho_a(\theta, \psi) \quad (14)$$

3.2.3 Overall crosslinking density

Given $\rho(\theta, \psi)$, the overall crosslinking density of the entire polymer at conversion ψ , is readily evaluated by integration above all possible values of birth conversion:

$$\bar{\rho}(\psi) = \frac{1}{\psi} \int_0^\psi \rho(\theta, \psi) d\theta \quad \theta \leq \psi \quad (15)$$

Through the overall crosslinking density it is possible to access other properties of the polymer network, such as the sol and gel partitioning and the molecular weight distribution between crosslinks, as briefly illustrated in the next section.

3.3 Sol and gel partitioning and molecular weight distribution between crosslinks

Sol and gel partitioning – Based on Flory's model, Tobita proposed to calculate the weight fraction of sol at every birth conversion.²⁹ Assuming that the crosslinking density is the same for all the primary chains born at the same conversion, Flory's original formula¹³ becomes equation (16):

$$w_s(\theta, \psi) = \sum_{n=1}^{\infty} f_w(n, \theta) \left(1 - \rho(\theta, \psi) (1 - w_s(\theta, \psi))\right)^n \quad (16)$$

Considering a primary chain of length n , this equation can be understood as follows:

- $(1 - w_s(\theta, \psi))$ represents the probability for a single unit of this chain not to be part of the sol (meaning to be part of the gel);
- multiplying by $\rho(\theta, \psi)$, provides the probability for the same unit to be crosslinked and part of the gel;
- thus $\left(1 - \rho(\theta, \psi) (1 - w_s(\theta, \psi))\right)^n$ is the probability that all the units of this chain of length n are not crosslinked with the gel, meaning they are part of the sol.

By introducing $f_w(n, \theta)$ from equation (5) into equation (16) and expanding the series, a polynomial equation was derived for w_s :²⁹

$$w_s(\theta, \psi) = AG_1 [T + ABG_1] \quad (17)$$

with $A = \alpha(\theta) / d(\theta, \psi)$, $T = \tau(\theta) / d(\theta, \psi)$, $B = \beta(\theta) / d(\theta, \psi)$, $d(\theta, \psi) = \alpha(\theta) + \rho(\theta, \psi) w_g(\theta, \psi)$ and $G_1 = 1 - \rho(\theta, \psi) w_g(\theta, \psi)$. The derivation of this equation is also reported by Sajjadi²⁷. Solving this equation at each value of θ , $w_s(\theta, \psi)$ is calculated, and the weight fraction of gel is readily obtained as:

$$w_g(\theta, \psi) = 1 - w_s(\theta, \psi) \quad (18)$$

From this equation the overall gel fraction at conversion ψ , $w_g(\psi)$, is evaluated by integration over all possible birth conversions, as already shown in equation (15).

Molecular weight distribution between crosslinks – Under the assumption of primary chains long enough to neglect end effects, Tobita³⁵ proposed the following equation for the molecular weight distribution between consecutive crosslinks:

$$f_w^c(n, \theta, \psi) = n \left(1 - \rho_{el}^f(\theta, \psi)\right)^{n-1} \rho_{el}^f(\theta, \psi)^2 \quad (19)$$

where ρ_{el}^f represents the elastic crosslinking density defined in terms of double bonds. In other words:

$$\rho_{el}^f = \rho_{el} / \left(1 + \rho_i + \rho_{cs,i} + \rho_{cp}\right) \quad (20)$$

$$\rho_{el}(\theta, \psi) = \rho(\theta, \psi) + \rho_{cs}(\theta, \psi) \quad (21)$$

and ρ_{el} is defined as the sum of the total crosslinking density and the secondary cyclization density. When increasing the crosslinking density, the elasticity decreases and the elastic modulus increases. Nevertheless the elastic crosslinking density does not account for physical crosslinkages which may play a role in the elastic properties. Therefore, it is not directly related to Young's elastic modulus characterizing the mechanical strength of the material.^{36, 37}

The zero and first-order moments of this distribution are readily evaluated from their definitions as:

$$\mu_0^c(\theta, \psi) = \sum_{n=1}^{\infty} \left(1 - \rho_{el}^f(\theta, \psi)\right)^{n-1} \rho_{el}^f(\theta, \psi)^2 \quad (22)$$

$$\mu_1^c(\theta, \psi) = \sum_{n=1}^{\infty} f_w^c(n, \theta, \psi) \quad (23)$$

These are instantaneous quantities: their corresponding cumulated values $\overline{\mu}_0^c(\psi)$ and $\overline{\mu}_1^c(\psi)$ are calculated by integration over all birth conversion values. Finally, the number average molecular weight between two consecutive crosslinks is expressed as:

$$M_n^c(\psi) = \frac{\overline{\mu}_1^c(\psi)}{\overline{\mu}_0^c(\psi)} M_n^0 \quad (24)$$

4 Parameter evaluation

The values of all model parameters used for the following simulations are listed in Table 4. The values of the kinetic parameters specific of the monomer/initiator system under examination (initiator dissociation rate constant k_d , crosslinking reactivity ratio r_3 and cyclization coefficients of primary (η_{cp}) and secondary cyclization (α_{cs})) were evaluated from experimental and literature data as explained below.

4.1 Initiator dissociation

The redox system TEMED/APS has been used in this work; despite the large popularity of this initiating system very few data are available in the literature. To estimate the initiator decomposition constant, a homopolymerization of Am in aqueous solution has been carried out. In particular, 2.5 mL solution with 10 % w/w of Am, 8.32 μ L APS (10 % w/w solution) and 16.8 μ L TEMED (10 % w/w solution) was polymerized at room temperature. The double bond consumption was monitored by UV spectroscopy at 286 nm as presented in Figure 3. Assum-

ing the pseudo-steady state assumption and a first order reaction with respect to APS, the initiation rate constant is evaluated from the slope at zero conversion through equation (25):

$$\left. \frac{d\psi}{dt} \right|_{t=0} = \frac{k_p}{\sqrt{k_t}} (2fk_d I_2)^{1/2} \quad (25)$$

Given $k_p^2 / k_t = 11.83 \text{ L / mol / s}$ for Am,³⁸ and assuming initiator efficiency f equal to 0.5, the dissociation rate constant of APS in the presence of TEMED at APS:TEMED ratio of 1:4 has been estimated as $k_d = 2.77 \times 10^{-5} \text{ s}^{-1}$. The advantage of employing such a decomposition rate constant is that all the elementary steps involved in the quite complex redox reaction involving APS and TEMED are lumped together.

FIGURE 3

4.2 Cross-propagation reaction

To evaluate the cross-propagation rate constants, $k_{p_{12}}$ and $k_{p_{21}}$, the values of the reactivity ratios (r_1 and r_2) as well as of the homopropagation rate constants, $k_{p_{11}}$ and $k_{p_{22}}$, are needed. These values have been found in the literature; note that the reactivity ratios were evaluated from composition data¹⁸ using the method of Kelen-Tüdös.³⁹ Concerning the propagation of pendant radicals, due to the lack of experimental information, equal reactivity of the double bonds has been assumed. This approximation, originally proposed by Flory,¹³ corresponds to assume $k_{p_{31}} = k_{p_{21}}$ and $k_{p_{32}} = k_{p_{12}}$. When dealing with small amounts of crosslinker, these two parameters do not play a decisive role because of the correspondingly small amounts of pendant radicals.

4.3 Crosslinking and secondary cyclization

The formation of a polymer network is mediated by two different reactions: the intermolecular attack of a radical chain to the PDB of another chain, i.e. crosslinking and the intramolecular secondary cyclization, where a backbone radical of one chain propagates till it attacks a PDB of the same chain. Secondary cyclization is accounted for by the parameter α_{cs} , whereas crosslinking by the kinetic constants $k_{p_{13}}, k_{p_{23}}$ and $k_{p_{33}}$. Employing the same hypothesis introduced by Landin and Macosko and defining $r_{ij} = k_{p_{ii}} / k_{p_{ij}}$, the following equality applies:³⁴

$$\frac{1}{r_{31}} = \frac{1}{2r_{32}} = r_{13} = \frac{r_{23}}{2} = r_3 \quad (26)$$

As a consequence, only two kinetic parameters need to be estimated, namely α_{cs} and r_3 . Their evaluation procedure has been proposed by Landin and Macosko³⁴ and relies on two types of experimental data: PDB conversion and gel point conversion.

Clearly, several combinations of α_{cs} and r_3 can be used to fit one of the two experimental information, but only one specific combination is able to satisfy both constraints at the same time. Employing the PDB conversion (for $w_c = 14\%$ and $w_c = 28\%$) and the gel points (for $w_c = 0.02\%$ and $w_c = 0.04\%$) reported by Tobita and Hamielec¹⁹ at 25°C, couples of r_3 and α_{cs} values were fitted to satisfy both conditions, namely comparing the predictions of gel point and the PDB conversion⁴⁰ (equations (27)-(29)) against the experimental data.

$$\frac{dD_3}{d\psi} = \frac{dD_3 / dM_2}{1 + dM_1 / dM_2} \quad (27)$$

$$\frac{dM_1}{dM_2} = \frac{r_{12}M_1(M_1 + M_2 / r_{12} + D_3 / r_{13})}{r_{21}M_2(M_1 / r_{21} + M_2 + D_3 / r_{23})} \quad (28)$$

$$\frac{dD_3}{dM_2} = (1 + \alpha_{cs}) \frac{D_3 r_{32} (M_1 / r_{31} + M_2 / r_{32} + D_3)}{M_2 r_{23} (M_1 / r_{21} + M_2 + D_3 / r_{23})} - (1 - \eta_{cp}) \quad (29)$$

Notably, equations ((27)-(29)) are fully equivalent to those shown in the appendix ((37)-(39)) and were re-written in this form to highlight the parameters to be estimated.

The solutions satisfying both constraints simultaneously are shown in Figure 4 as the shaded area resulting from the intersection of the four calculated curves (PDB conversion for $w_c = 28\%$ and $w_c = 14\%$ and gel point constraints applied for both $w_c = 0.02\%$ and $w_c = 0.04\%$). Ideally, the four curves should be two, one for the gel point and one for the PDB conversion, independent from the crosslinker amount, thus leading to only one single pair of values. However, due to the experimental error, a range of pair values is identified, highlighted by the shaded area shown in Figure 4: such area is quite narrow, allowing thus an accurate estimation of r_3 and α_{cs} . In particular, the following two values have been selected: $r_3 = 5.76$ and $\alpha_{cs} = 7.61$. It is worth noticing that this parameter evaluation has been carried out assuming the primary cyclization coefficient η_{cp} equal to 0.81. This value has been obtained by Tobita and Hamielec¹⁹ and Naghash and Okay²⁰ by fitting their own experimental data at low conversion.

FIGURE 4

It is worth mentioning that Tobita and Hamielec¹⁹ reported values of r_3 and α_{cs} in the order of 10^3 , hence quite different from those estimated here employing the mentioned fitting procedure,³⁴ although the authors themselves consider their parameter evaluation quite poor. Despite the parameter discrepancy, the mechanism of Am/BAm network formation is invariably

dominated by secondary cyclization (i.e. $\alpha_{cs} > 1$). Moreover, defining $k_{p3}^T = k_{p3}^* (1 + \alpha_{cs})$ as the sum of crosslinking and secondary cyclization and estimating the ratio $k_{p3}^T / (k_{p1}^* + k_{p2}^*)$, values in the order of 10^0 are obtained, as also stated by Tobita and Hamielec: this confirms that the overall PDB consumption is predicted in the very same way despite the largely different absolute values of the parameters r_3 and α_{cs} .

To further confirm the reliability of our estimation, the gel fraction against conversion for $w_c = 0.04\%$ calculated using our parameter values (continuous line) and Tobita and Hamielec parameter values¹⁹ (dashed line) is shown in Figure 5. Notably, the values of the initiation parameters have been found in the literature,²⁹ whereas equation (16) has been employed to estimate the gel curve. While the gelation onset is predicted at 11% of conversion in the first case, in very good agreement with the experimental data by Tobita and Hamielec,¹⁹, no gelation at all is predicted using the larger r_3 and α_{cs} values previously suggested in the literature. This can be explained considering that $r_3 \cong 10^3$ indicates crosslinking reactions 3 orders of magnitude slower than propagation, thus suppressing gel formation.

FIGURE 5

4.4 Intramolecular cyclization

The primary cyclization coefficient, η_{cp} , has been determined from swelling measurements, taking advantage of the well-known Flory-Rehner²² equation:

$$\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 = -\frac{v_m^0 d_p}{M_n^c} \left(\phi_p^{1/3} \phi_0^{2/3} - \frac{\phi_p}{2} \right) \quad (30)$$

where ϕ_p is the volume fraction of the polymer in the mixture with the swelling solvent at equilibrium, χ is the Flory-Huggins interaction parameter, v_m^0 is the molar volume of the solvent, ϕ_0 is the volume fraction of polymer at preparation and d_p the polymer density. A simple equation to compute the average molecular weight between two consecutive crosslinks involving the primary cyclization coefficient has been proposed by Okay:²¹

$$\frac{M_n^c}{M_n^0} = \frac{1}{2X(1-\eta_{cp})} \quad (31)$$

with X being the initial ratio between Am and BAm. Combining the last two equations, and making η_{cp} explicit, the following relationship providing η_{cp} as a function of the measurable quantity ϕ_p is finally obtained:

$$\eta_{cp} = 1 - \frac{M_n^0}{v_m^0 d} \frac{\ln(1-\phi_p) + \phi_p + \chi\phi_p^2}{2X \left(\frac{\phi_p}{2} - \phi_p^{1/3} \phi_0^{2/3} \right)} \quad (32)$$

This equation will be used in the next section to evaluate η_{cp} from the swelling data summarized in Table 2.

4.5 Termination reaction

In the present model, diffusion-controlled termination rate constants have been considered; specifically, the kinetic expression suggested by Buback et al.⁴¹ was selected:

$$k_{t_{ii}} = \frac{1}{\frac{1}{k_{t_{ii}}^{chem}} + \frac{\exp(C_{\eta_i} w_t \psi)}{k_{t,Di}^0}} + C_{RD,i} k_{p_{ii}} (1-\psi) \quad (33)$$

Such equation has been applied for homo-terminations; the cross termination rate constants have been estimated as geometric averages:

$$k_{t_{ij}} = \sqrt{k_{t_{ii}} k_{t_{jj}}} \quad (34)$$

Notably, the values of $C_{\eta i}$, C_{RDi} and k_{t,D_i}^0 have been considered equal for all radicals and have been selected from the ranges suggested by Buback et al.,⁴¹⁻⁴³ as no estimates of those parameters were found in the literature for this specific system. In particular, $C_{\eta i} = 27$, (literature range: 10-27), $C_{RDi} = 250$ (literature range 94-1900) and $k_{t,D_i}^0 = 2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ were chosen. Notably, these values were selected to give a termination rate constant at zero conversion which lies in between the termination rate constants of Am and BAm (Table 4).

Finally, since the values of the termination rate constants for the radicals on PDB are not easily accessible, the termination rate constant is set equal to the one of the monovinyl monomer, i.e.:

$$k_{t_{33}} = k_{t_{11}} \quad (35)$$

5 Results and discussion

5.1 Simulation of Am/BAm copolymerization

The comparison of the model predictions to the experimental data was done at different amounts of crosslinker ($w_c = 3\%, 4\%$ and 5%) and different monomer concentrations ($w_t = 3-16\%$) In addition to predicting quantities directly comparable to the experimental results, the model can be used to calculate properties not measured experimentally, such as the crosslinking density, or the CLD of “primary chains” in the gel polymer. The two latter quan-

tities provide unique information towards a better understanding of the synthesized hydrogel microstructure.

As previously mentioned, swelling data were used to estimate the primary cyclization coefficient, η_{cp} . This coefficient is expected to be affected by the dilution of the monomer mixture. The higher the dilution, the higher the probability of intramolecular compared to intermolecular reactions. The primary cyclization coefficient is calculated from equation (32) using the results of the three series of experiments ($w_c = 3-5\%$). An empirical fitting is then proposed to describe the variation of the primary cyclization coefficient with the monomer concentration, w_t :

$$\eta_{cp} = \exp(-3.356w_t^2) \quad (36)$$

The final results are presented in Figure 6; as already noticed by Tobita,²⁹ the amount of crosslinker has little effect on the primary cyclization coefficient in this range of concentrations. A significant role of the primary cyclization reaction is expected in the system under examination, as already observed in the literature.^{20, 21} At low monomer concentration ($w_t = 3\%$) the fraction of PDBs involved in primary cyclization reaches 99.5%; this means that, even though less than 1% of the potential PDBs is actually available for crosslinking reactions, complete gelation of the polymer network can be achieved. On the other hand, the primary cyclization coefficient decreases to 91% when the monomer concentration increases up to 16%.

FIGURE 6

Using the empirical expression for η_{cp} introduced above, the comparison between experimental and model predicted swelling ratios (employing equation (30)) is obtained (cf. Figure 7). The agreement is generally good, particularly at the highest concentrations; discrepancies appear at high dilution, where the model under-predicts the swelling ratios. However, it should be mentioned that the swelling ratios observed experimentally at very low amount of monomer are extremely large and therefore difficult to measure because the gel slices are really soft. This behaviour is even more pronounced when the concentration of crosslinker is also low; therefore, the reliability of these measurements is quite questionable. Figure 7 also shows how the swelling ratio decreases when increasing monomer concentration, i.e. stronger gels are obtained with concentrated systems. These results confirm the impact of the system dilution on the primary cyclization reactions and, in turn, on the properties of the gel. As suggested by the plateau reached at the highest concentrations, the competition between intra- and intermolecular reactions tends to favour the latter and the effect of the dilution becomes less important at high concentration. Thus summarizing, the polymer network structure is not only dependent on the relative concentration of divinyl monomer with respect to that of the monovinyl monomer (w_c) but also on the absolute value of the concentration of the monomer mixture (w_t).

FIGURE 7

Notably, the η_{cp} estimated from our swelling measurements is always comprised between 0.9 and 0.99, in agreement with Okay et al.,²¹ whereas Tobita and Hamielec¹⁹ and Naghash and Okay²⁰ reported the smaller value 0.81, estimated employing titration measurements. This discrepancy can be probably explained reminding that pre-gel soluble polymer was used for

the titration in the latter cases, whereas swelling measurements on the gel were performed in this paper and in Okay et al.²¹ In particular, cyclization reactions are expected to be really significant at high conversion in the gel because of monomer depletion, while the primary cyclization coefficient obtained by titration of the sol polymer PDB is extrapolated at zero conversion. As a matter of fact, Stockmayer¹⁵ was already suggesting not to use the statistical approach (at that time still neglecting cyclization) in the post gelation period because cyclization reactions at high conversion could generate a major difference between sol and gel polymer.

5.2 Validation of the model

In order to provide a general model validation as well as check the reliability of the estimated parameter values, different swelling data published by Okay et al.²¹ are finally simulated (i.e. predicted) using the estimated parameters. Experimental results are reported at $w_t = 5\%$ and different amounts of divinyl monomer ($w_c = 0.7\% - 15\%$). The η_{cp} value of 0.99 estimated from equation (36) at this monomer concentration is comparable to the value of 0.95 already proposed by Okay et al.²¹ and leads to good predictions, as shown in Figure 8.

FIGURE 8

In Figure 8 the prediction obtained with $\eta_{cp} = 0$ is also reported, in order to appreciate that primary cyclization has to be accounted for to obtain correct predictions. Moreover, the predictions employing the value $\eta_{cp} = 0.81$, suggested by Tobita and Hamielec¹⁹ and Naghash and Okay²⁰, is also reported: it is confirmed that the suggested value of 0.81 can be employed

only in the pre-gel regime, otherwise leading to erroneous predictions of the gel properties. The results obtained by Tobita and Hamielec,¹⁹ by Naghash and Okay,²⁰ by Okay et al.²¹ and in the present paper, indicate that the primary cyclization is most likely a conversion-dependent reaction, with an increased relevance along the reaction coordinate.

5.3 Parametric calculations

The parameters provided in the present work can be used to control the hydrogel structure for Am/BAm systems. By properly tuning the total monomer concentration w_t , the efficiency of cyclization will be affected (equation (36)), leading to changes both in the crosslinking density structure as well as in the gel conversion. A set of parametric calculations has been performed to clarify the impact of η_{cp} on the gel properties: the results are reported in Figure 9 (gel fraction) and Figure 10 (crosslinking density).

FIGURE 9

FIGURE 10

As expected, when increasing w_t (from 12% to 30%) the efficiency of primary cyclization is reduced, therefore more PDB are available for crosslinking, resulting in the anticipated gelation shown in Figure 9. The same reasoning can explain the trends observed in Figure 10: when increasing w_t , more PDB are consumed via crosslinking reactions, leading to larger values in the crosslinking densities of both the sol and gel phase.

The impact of changing the total monomer concentrations can be further appreciated when calculating the primary and the elastic crosslinking densities versus conversion (equation (10) and (21), respectively). Employing the aforementioned range of w_t , these quantities are calculated and shown in Figure 11.

FIGURE 11

Once more, by increasing the total monomer concentration, the crosslinking reaction consumes more PDB than the primary cyclization, leading to an increase in the elastic crosslinking density (hence to a stiffer gel) and to a decrease in primary cyclization density. The latter findings not only prove the soundness of the estimated parameters but also indicate that the final network structure can be tuned by changing the total monomer concentration.

6 Conclusions

New parameter values for the reactions of crosslinking and intramolecular cyclization have been estimated for the solution copolymerization of Am/BAm, using the probabilistic model proposed by Tobita and Hamielec,²³ an effective tool for the simulation of kinetically controlled copolymerization processes. In particular, an empirical expression as a function of the overall content of monomer mixture is proposed for the primary cyclization efficiency (η_{cp}), by fitting model predictions against our own experimental data of swelling for hydrogels produced at three different weight fractions of divinyl monomer (3-5%) and fourteen monomer weight fractions (3-16%). Finally, the general reliability of the estimated parameter values and of the selected modelling approach is proved by comparison with literature data for the same copolymerization system: the average molecular weight between consecutive crosslinks is well predicted using the η_{cp} value as estimated through the empirical relationship developed in this work. Finally, parametric simulations showed the impact of primary cyclization on the hydrogel properties.

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Nomenclature

| | | |
|------------------------|-----------------------|--|
| A | — | Kinetic parameter |
| B | — | Kinetic parameter |
| C_η | — | Viscosity coefficient in the termination kinetic constant |
| C_{RD} | — | Propagational growth in the termination kinetic constant |
| d_p | $g\ cm^{-3}$ | Polymer density |
| d_w | $g\ cm^{-3}$ | Water density |
| D_3 | $mol\ L^{-1}$ | Pendant double bonds concentration |
| f | — | Initiator efficiency |
| f_n | — | Primary molecules number CLD |
| f_w | — | Primary molecules weight CLD |
| f_w^{sol}, f_w^{gel} | — | Primary molecules weight CLD of the sol/gel |
| f_w^c | — | Primary molecules weight CLD between crosslinks |
| G_k | — | Kinetic parameters |
| I_2^0, I_2 | $mol\ L^{-1}$ | Initial/present initiator concentration |
| k_d | s^{-1} | Initiator dissociation rate constant |
| $k_{p_{ij}}$ | $L\ mol^{-1}\ s^{-1}$ | Propagation rate constant of type i radical with the monomer of type j |
| $k_{p_i}^*$ | $L\ mol^{-1}\ s^{-1}$ | Pseudo-homogeneous propagation rate constant of the monomer i |
| $k_{t_{ij}}$ | $L\ mol^{-1}\ s^{-1}$ | Termination rate constant |
| k_{tc}, k_{td} | $L\ mol^{-1}\ s^{-1}$ | Combination/Disproportionation rate constant |
| $k_{t,D}^0$ | $L\ mol^{-1}\ s^{-1}$ | Purely diffusion controlled termination rate constant |
| k_t^* | $L\ mol^{-1}\ s^{-1}$ | Pseudo-homogeneous termination rate constant |
| $m_{polymer}$ | g | Mass of the slice of gel after immersion in water |

| | | |
|----------------------------------|----------------|--|
| $m_{polymer}^{dry}$ | g | Mass of the dried slice of polymer |
| M_1^0, M_2^0 | $mol L^{-1}$ | Initial concentration of monomers 1 and 2 |
| M_1, M_2 | $mol L^{-1}$ | Concentration of monomers 1 and 2 |
| M_n^0 | $g mol^{-1}$ | Molecular weight of the repeated unit |
| M_n^c | $g mol^{-1}$ | Average molecular weight between consecutive crosslinks |
| n | — | Number of unit in the polymer chain |
| $P_{m,n}$ | $mol L^{-1}$ | Concentration of dead chains of length m and n divinyl monomers |
| q | — | Swelling ratio (w/w) |
| $R_{i,m,n}$ | $mol L^{-1}$ | Concentration of growing chains of length m and n divinyl monomers with a radical center on a type i monomer (1, 2 or 3) |
| R_{tot} | $mol L^{-1}$ | Total concentration of radicals |
| r_{ij} | — | Reactivity ratios |
| T | — | Kinetic parameter |
| v_m^0 | $m^3 mol^{-1}$ | Molar volume of the solvent |
| w_g, w_s | — | Instantaneous weight fraction of gel/sol |
| $\overline{w_g}, \overline{w_s}$ | — | Cumulative weight fraction of gel/sol |
| w_c | — | Initial weight fraction of crosslinker |
| w_i | — | Initial weight fraction of monomers |
| x_1, x_2 | — | Molar fraction of monomer types 1 and 2 |
| X | — | Divinyl to monovinyl monomer molar ratio |

Greek letters

| | | |
|-------------------------------|---|---|
| α | — | Kinetic ratio |
| α_{cs} | — | Secondary cyclization coefficient |
| β | — | Kinetic ratio |
| Γ_1 | — | Kinetic parameter |
| η_{cp} | — | Primary cyclization coefficient |
| θ | — | Birth conversion |
| $\mu_k^c, \overline{\mu}_k^c$ | — | Instantaneous and Cumulative k^{th} order moment of the CLD between consecutives crosslinks |
| μ_k | — | k^{th} order moment of the primary polymer CLD |
| $\rho, \overline{\rho}$ | — | Instantaneous and Cumulative total crosslinking density |
| ρ_a, ρ_i | — | Additional and Instantaneous crosslinking density |
| $\rho^f, \overline{\rho}^f$ | — | Instantaneous and Cumulative total crosslinking density with respect to the number of units |
| ρ_{cp} | — | Primary cyclization density |

| | | |
|---------------------------------------|---|---|
| $\rho_{cs,a}, \rho_{cs,i}$ | — | Additional and Instantaneous secondary cyclization density |
| $\rho_{el}, \overline{\rho_{el}}$ | — | Instantaneous/Cumulative elastic crosslinking density |
| $\rho_{el}^f, \overline{\rho_{el}^f}$ | — | Instantaneous/Cumulative elastic crosslinking density with respect to the number of units |
| τ | — | Kinetic ratio |
| ϕ_i | — | Fraction of radical of type i |
| ϕ_p | — | Volume fraction of polymer |
| χ | — | Flory-Huggins interaction parameter |
| ψ | — | Present conversion |
| | — | |

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Appendix

The most typical free-radical polymerization kinetic scheme involving initiator decomposition, propagation, and bimolecular terminations both by combination and disproportionation is complemented by additional reactions peculiar for monovinyl/divinyl copolymerizations. Notably crosslinking reactions and two different types of cyclization are accounted for. The final kinetic scheme is shown in Table 3. The meaning of all symbols is reported in the Nomenclature. All the rate constants are assumed to be conversion-independent, except for the termination rate constants. This model involves three types of monomers and three types of radicals as sketched in Table 2. The mass balances for each monomer species, when considering well mixed, isothermal batch reactor are derived in equations (37) to (39):

$$\frac{dM_1}{d\psi} = -\frac{k_{p_1}^* M_1}{k_{p_1}^* M_1 + k_{p_2}^* M_2} (M_1^0 + M_2^0) \quad (37)$$

$$\frac{dM_2}{d\psi} = -\frac{k_{p_2}^* M_2}{k_{p_1}^* M_1 + k_{p_2}^* M_2} (M_1^0 + M_2^0) \quad (38)$$

$$\frac{dD_3}{d\psi} = \left(\frac{(1 - \eta_{cp}) k_{p_2}^* M_2}{k_{p_1}^* M_1 + k_{p_2}^* M_2} - \frac{(1 + \alpha_{cs}) k_{p_3}^* D_3}{k_{p_1}^* M_1 + k_{p_2}^* M_2} \right) (M_1^0 + M_2^0) \quad (39)$$

To get rid of the total concentration of radicals the equations are written with respect to monomer conversion $\psi = \frac{M_1^0 + M_2^0 - M_1 - M_2}{M_1^0 + M_2^0}$. The time derivative of the conversion is given by

equation (40).

$$\frac{d\psi}{dt} = \frac{(k_{p_1}^* M_1 + k_{p_2}^* M_2) R_{tot}}{(M_1^0 + M_2^0)} \quad (40)$$

where $R_{tot} = \sqrt{\frac{2fk_d I_2}{k_t^*}}$ is the total concentration of radicals and $I_2 = I_2^0 e^{-k_d t}$ the concentration of initiator.

The so-called pseudo-kinetic approach is used;⁴⁴ accordingly the kinetic parameters propagation ($k_{p_i}^*$) and termination (k_t^*) are expressed as effective rate constants, defined as:

Propagation

$$k_{p_1}^* = k_{p_{11}} \phi_1 + k_{p_{21}} \phi_2 + k_{p_{31}} \phi_3 \quad (41)$$

$$k_{p_2}^* = k_{p_{12}} \phi_1 + k_{p_{22}} \phi_2 + k_{p_{32}} \phi_3 \quad (42)$$

$$k_{p_3}^* = k_{p_{13}} \phi_1 + k_{p_{23}} \phi_2 + k_{p_{33}} \phi_3 \quad (43)$$

Termination

$$k_t^* = k_{t_{11}} \phi_1^2 + k_{t_{22}} \phi_2^2 + k_{t_{33}} \phi_3^2 + 2k_{t_{12}} \phi_1 \phi_2 + 2k_{t_{13}} \phi_1 \phi_3 + 2k_{t_{23}} \phi_2 \phi_3 \quad (44)$$

$$k_t^* = k_{tc}^* + k_{td}^* \quad (45)$$

The pseudo-kinetic parameters are composition-dependent and require the computation of the radical mole fractions, ϕ_i . The fraction of each radical is computed assuming quasi-steady-state (QSS) for all the active species. This assumption has to be seen with particular caution since Okay⁴⁵ reported a stability of several month for radicals in the gel phase. However, due to the difficulty to properly quantify their reduced reactivity in gel, it has been used in the present case as well.^{16, 23} The radical fractions are calculated solving the following system:

$$\left. \begin{aligned}
& - \begin{bmatrix} k_{p_{12}} M_2 + k_{p_{13}} D_3 + \\ \eta_{cp} k_{p_{12}} M_2 \\ + \alpha_{cs} k_{p_{13}} D_3 \end{bmatrix} \phi_1 + \begin{bmatrix} k_{p_{21}} M_1 \end{bmatrix} \phi_2 + \begin{bmatrix} k_{p_{31}} M_1 \end{bmatrix} \phi_3 = 0 \\
& \begin{bmatrix} k_{p_{12}} M_2 \end{bmatrix} \phi_1 - \begin{bmatrix} k_{p_{21}} M_1 + k_{p_{23}} D_3 \\ \eta_{cp} k_{p_{22}} M_2 \\ + \alpha_{cs} k_{p_{23}} D_3 \end{bmatrix} \phi_2 + \begin{bmatrix} k_{p_{32}} M_2 \end{bmatrix} \phi_3 = 0 \\
& \phi_1 + \phi_2 + \phi_3 = 1
\end{aligned} \right\} \quad (46)$$

Where η_{cp} and α_{cs} are the coefficients of primary and secondary cyclization respectively.

Table 1 Reaction recipes.

| Am | BAm | Tot | TEMED/APS | Am | BAm | Tot | TEMED/APS | Am | BAm | Tot | TEMED/APS |
|---------------|-------------------|-------|-----------|---------------|-------------------|-------|-----------|---------------|-------------------|-------|-----------|
| g | gx10 ² | g | μL | g | gx10 ² | g | μL | g | gx10 ² | g | μL |
| $w_c^0 = 3\%$ | | | | $w_c^0 = 4\%$ | | | | $w_c^0 = 5\%$ | | | |
| 0.87 | 2.7 | 30.02 | 20/100 | 1.73 | 7.2 | 59.97 | 40/200 | 0.85 | 4.5 | 30.03 | 20/100 |
| 1.16 | 3.7 | 30.08 | 20/100 | 2.31 | 9.2 | 60.02 | 40/200 | 1.14 | 5.9 | 29.98 | 20/100 |
| 1.46 | 4.5 | 30.16 | 20/100 | 2.88 | 11.8 | 59.99 | 40/200 | 1.42 | 7.4 | 30.00 | 20/100 |
| 1.75 | 5.5 | 30.07 | 20/100 | 3.46 | 14.2 | 59.93 | 40/200 | 1.71 | 9.1 | 30.04 | 20/100 |
| 2.04 | 6.3 | 30.03 | 20/100 | 4.03 | 16.7 | 60.04 | 40/200 | 2.00 | 10.6 | 29.98 | 20/100 |
| 4.65 | 14.6 | 60.01 | 40/200 | 4.60 | 19.2 | 60.07 | 40/200 | 2.28 | 11.8 | 30.01 | 20/100 |
| 2.62 | 8.1 | 30.08 | 20/100 | 5.19 | 21.5 | 60.02 | 40/200 | 2.56 | 13.7 | 30.01 | 20/100 |
| 2.91 | 9.0 | 30.07 | 20/100 | 5.77 | 24.1 | 60.00 | 40/200 | 2.85 | 15.2 | 30.06 | 20/100 |
| 3.21 | 10.0 | 30.03 | 20/100 | 6.34 | 26.3 | 60.03 | 40/200 | 3.13 | 16.7 | 30.02 | 20/100 |
| 3.49 | 10.7 | 30.01 | 20/100 | 6.92 | 28.5 | 60.07 | 40/200 | 3.42 | 17.9 | 30.05 | 20/100 |
| 3.78 | 11.7 | 30.08 | 20/100 | 7.49 | 31.5 | 60.12 | 40/200 | 3.70 | 19.5 | 30.10 | 20/100 |
| 4.08 | 12.6 | 30.01 | 20/100 | 8.07 | 33.6 | 60.03 | 40/200 | 3.99 | 21.3 | 30.11 | 20/100 |
| 4.36 | 13.3 | 30.09 | 20/100 | 8.65 | 35.9 | 60.08 | 40/200 | 4.28 | 22.5 | 30.03 | 20/100 |
| 4.66 | 14.7 | 30.04 | 20/100 | 9.21 | 38.4 | 60.07 | 40/200 | 4.56 | 24.2 | 30.04 | 20/100 |

Table 2 Chemical species involved in the model.






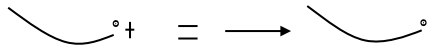
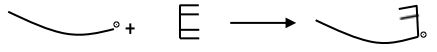
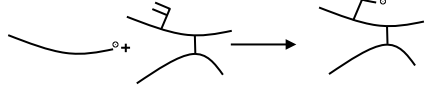
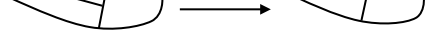

| | 1 | 2 | 3 |
|----------------|---|---|---|
| Monomer | = |  |  |
| Radical |  |  |  |

Table 3 Free-radical copolymerization kinetic scheme.

| | | |
|------------------------------|--|---|
| Initiation | $I_2 + 2M_1 \xrightarrow{fk_d} 2R_{1,1,0}^\cdot$ | |
| | $I_2 + 2M_2 \xrightarrow{fk_d} 2R_{2,1,1}^\cdot$ | |
| Propagation | $R_{i,m,n}^\cdot + M_1 \xrightarrow{k_{pi1}} R_{1,m+1,n}^\cdot$ |  |
| | $R_{i,m,n}^\cdot + M_2 \xrightarrow{k_{pi2}} R_{2,m+1,n+1}^\cdot$ |  |
| | $R_{i,m,n}^\cdot + D_{3,r,q} \xrightarrow{k_{pi3}} R_{3,m+r,n+q-1}^\cdot$ |  |
| Primary cyclization | $R_{i,m,n}^\cdot \xrightarrow{n_{cp}} R_{3,m,n-1}^\cdot$ |  |
| Secondary cyclization | $R_{i,m,n}^\cdot + D_{3,r,q} \xrightarrow{\alpha_{cs}} R_{3,m+r,n+q-1}^\cdot$ |  |
| Termination | $R_{i,m,n}^\cdot + R_{j,r,q}^\cdot \xrightarrow{k_{tij}} \begin{cases} P_{m+r,n+q} \\ P_{m,n} + P_{r,q} \end{cases}$ | |

$R_{i,m,n}^\cdot$
 $\begin{cases} i = \text{radical type (1 = monovinyl, 2 = divinyl, 3 = pendant)} \\ m = \text{chain length} \\ n = \text{PDB} \end{cases}$

Table 4 Value of the kinetic parameters used for the simulation (T = 25°C).

| Kinetic parameters | Value | Reference |
|--------------------|--|--------------------------------|
| f | 0.5 | - |
| k_d | $2.770 \cdot 10^{-5} s^{-1}$ | this work |
| k_{p11} | $1.800 \cdot 10^4 L \cdot mol^{-1} \cdot s^{-1}$ | Dainton, 1956 ⁴⁶ |
| k_{p22} | $3.912 \cdot 10^4 L \cdot mol^{-1} \cdot s^{-1}$ | Gopalan, 1983 ⁴⁷ |
| r_{12} | 0.57 | Baselga, 1989 ¹⁸ |
| r_{21} | 3.40 | Baselga, 1989 ¹⁸ |
| r_3 | 5.76 | this work |
| $k_{tc_{ii}}$ | 0.0 | Giz, 2001 ³⁸ |
| k_{td11} | $1.013 \cdot 10^7 L \cdot mol^{-1} \cdot s^{-1}$ | Giz, 2001 ³⁸ |
| k_{td22} | $3.437 \cdot 10^8 L \cdot mol^{-1} \cdot s^{-1}$ | Gupta, 1994 ⁴⁸ |
| η_{cp} | $\exp(-3.356w_t^2)$ | this work |
| α_{cs} | 7.61 | this work |
| $k_{tD,0}$ | $2.0 \cdot 10^8 L \cdot mol^{-1} \cdot s^{-1}$ | Buback et al. ⁴¹⁻⁴³ |
| C_η | 27 | |
| C_{RD} | 250 | |
| χ | 0.48 | Baselga, 1989 ¹⁸ |
| d_p | $1.35 \text{ g} \cdot \text{cm}^3$ | Okay, 1997 ²¹ |
| d_w | $1.0 \text{ g} \cdot \text{cm}^3$ | - |
| v_m^0 | $18 \text{ cm}^3 \cdot \text{mol}^{-1}$ | - |
| M_n^0 | $71 \text{ g} \cdot \text{mol}^{-1}$ | - |

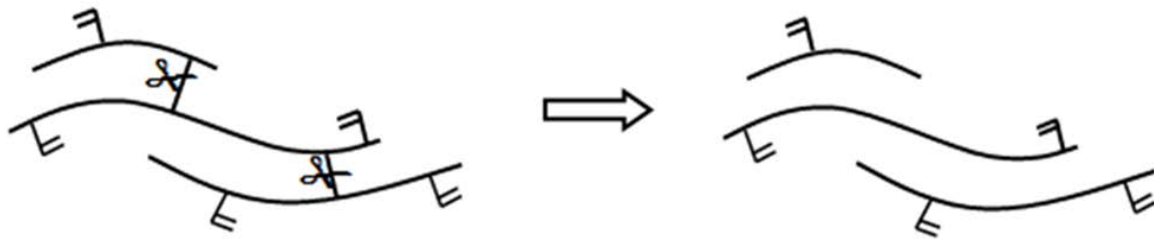


Figure 1 Primary chains are formed by severing the crosslinks in a polymer network.

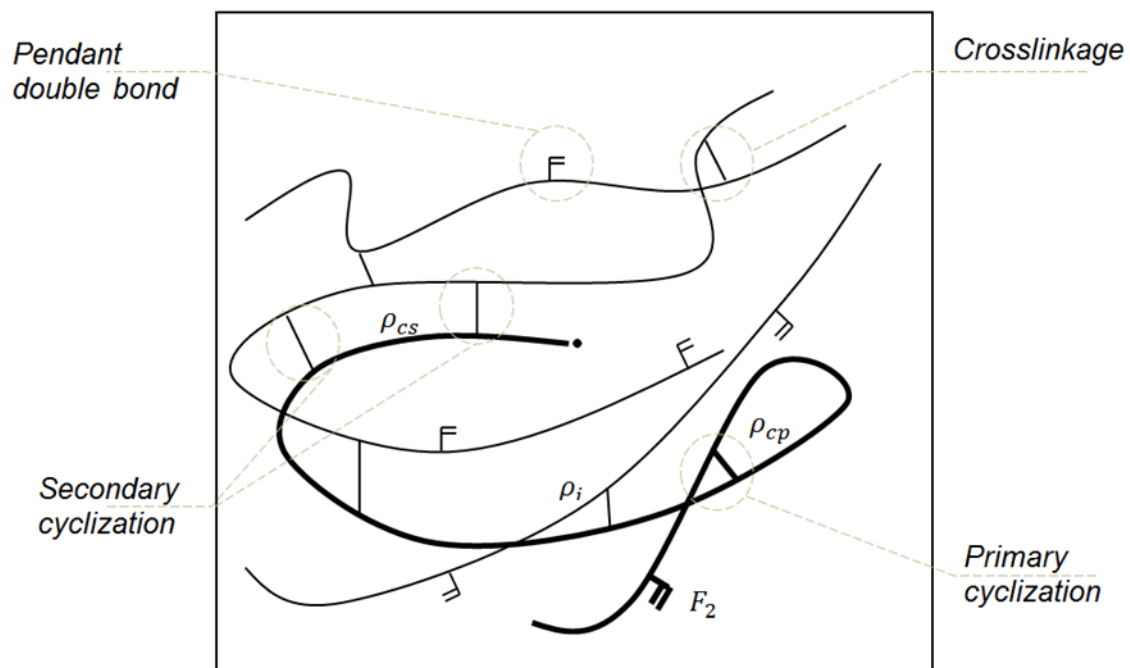


Figure 2 Nomenclature used in the model.

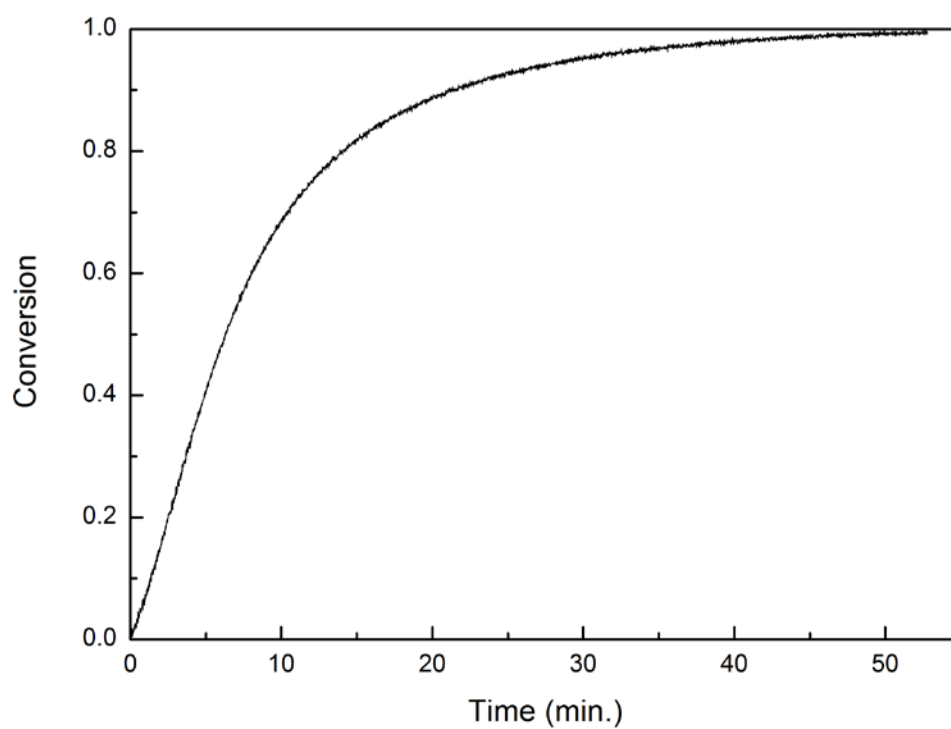


Figure 3 Conversion of Am during the polymerization reaction; consumption of double bonds monitored by UV spectroscopy.

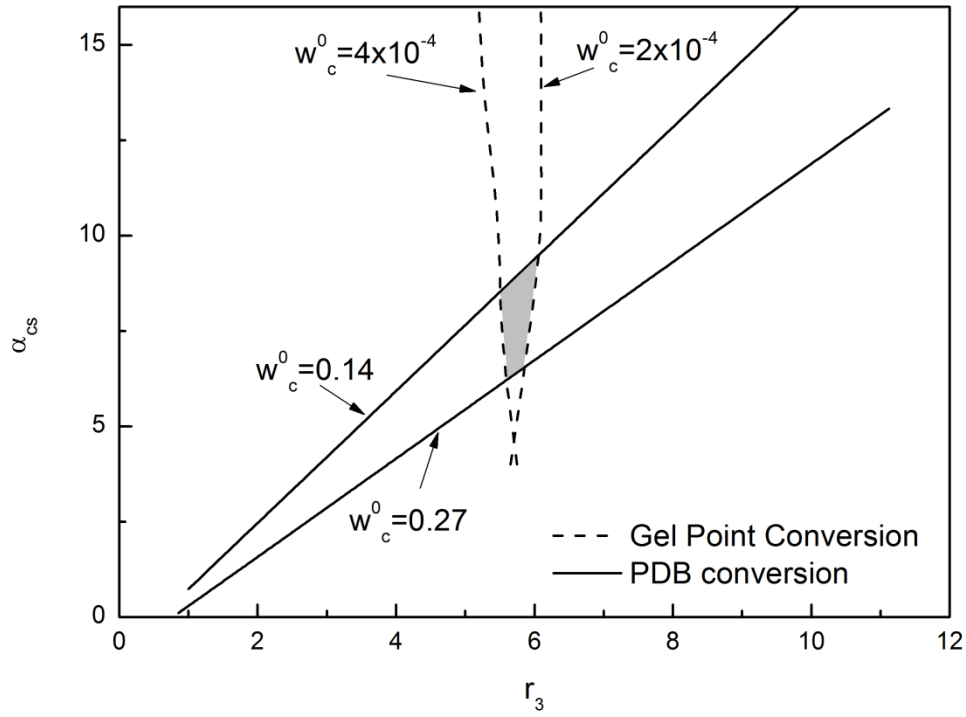


Figure 4 Graphical determination of r_3 and α_{cs} according to the procedure described by Landin and Macosko.³⁴ “Gel point conversion” (dashed lines) represent all the (r_3, α_{cs}) pairs satisfying the constraints on the gel point conversion. “PDB conversion” (continuous lines) represent (r_3, α_{cs}) pairs satisfying the constraint on the PDBs conversion. The shaded area obtained by the intersection of the four curves corresponds to the set of parameters r_3 and α_{cs} satisfying both constraints simultaneously.

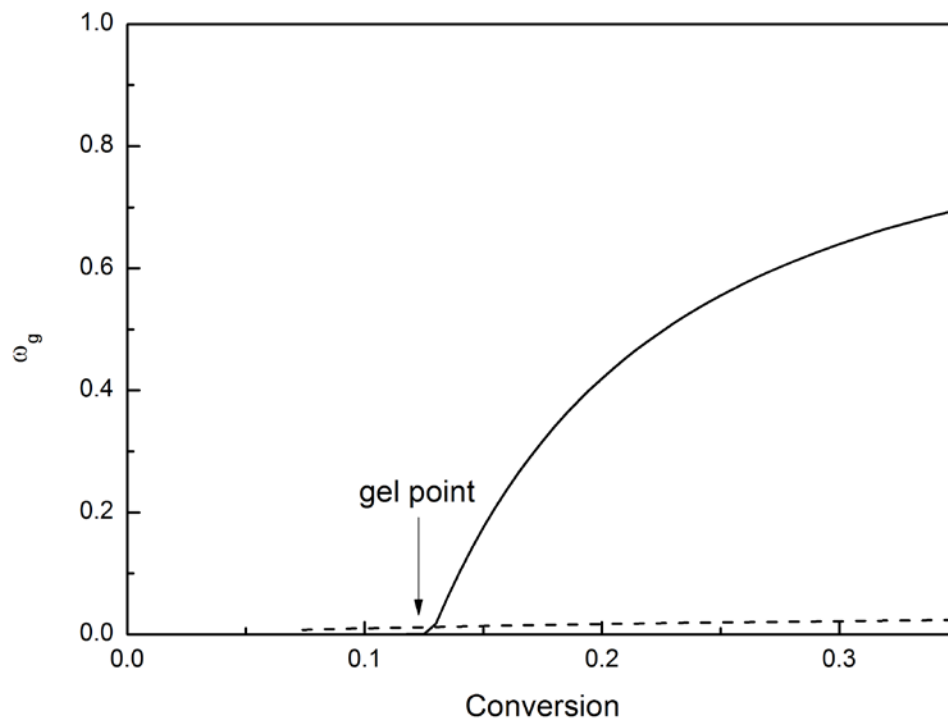


Figure 5 Gel fraction against conversion predicted for the case $w_c = 0.04\%$ employing α_{cs} and r_3 values evaluated by fitting in this work (continuous line) and proposed by Tobita and Hamielec¹⁹ (dashed line). The experimental gel point reported by Tobita and Hamielec is at 11% of conversion.

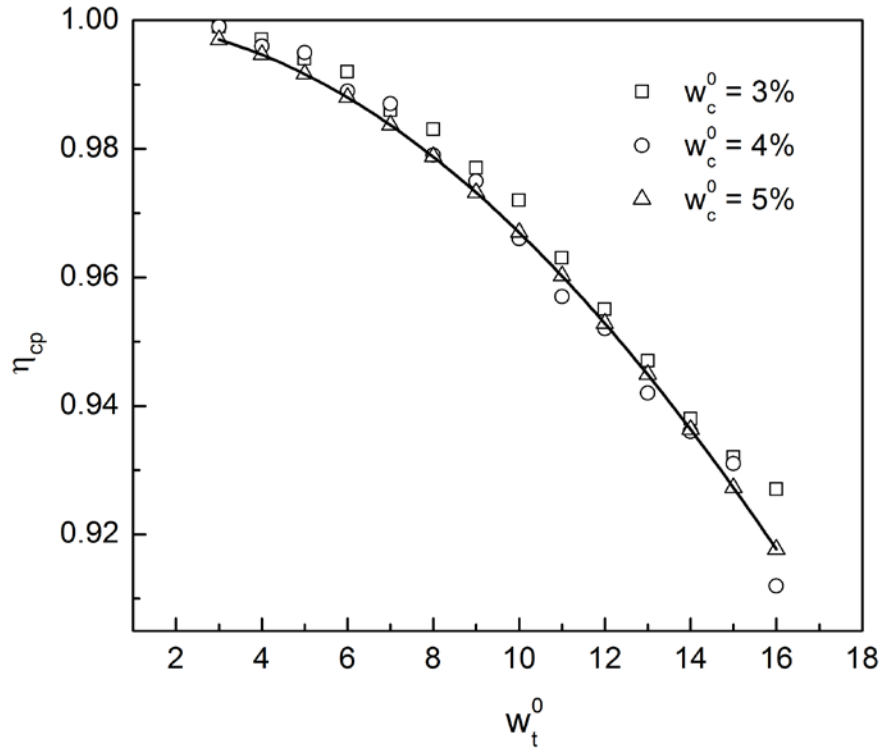


Figure 6 Estimated value of η_{cp} as a function of the monomer weight fraction for three different amounts of crosslinker, w_c . The line corresponds to the fitting equation $\eta_{cp} = \exp(-3.356 w_t^2)$.

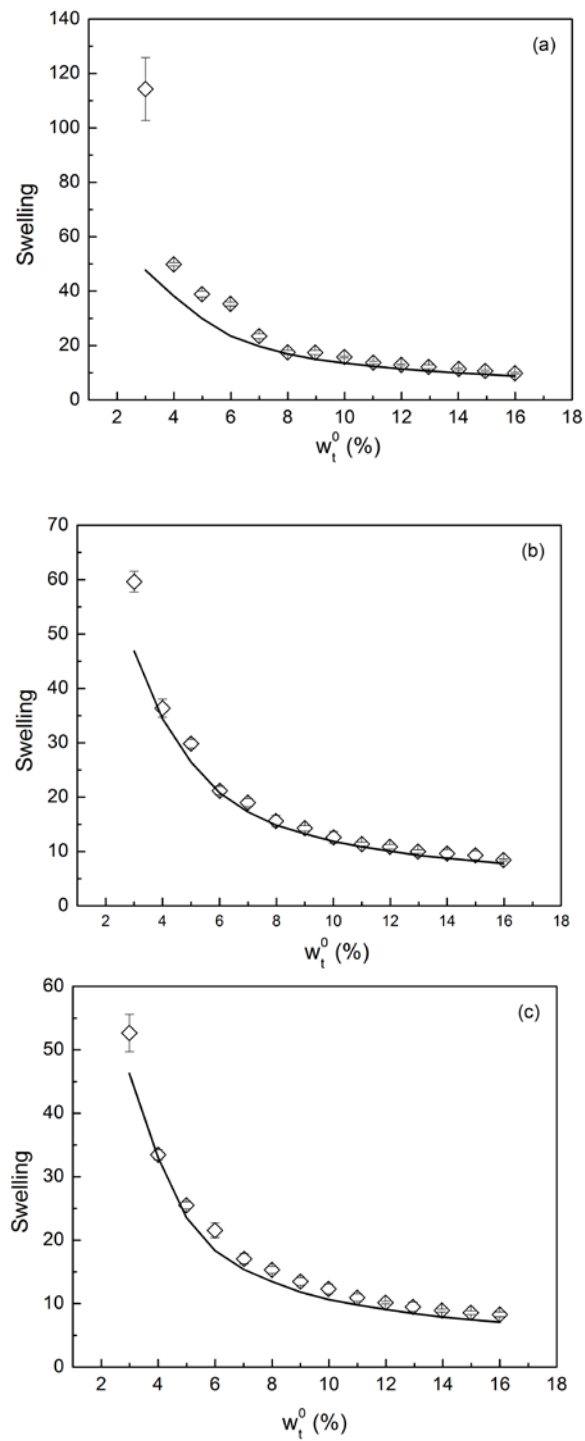


Figure 7. Swelling ratio versus monomer weight fraction for different amounts of crosslinker ($w_c =$ (a) 3%, (b) 4% and (c) 5%). Continuous lines represent model prediction; symbols are experimental values. Error bars represent the standard deviation of 8 different samples.

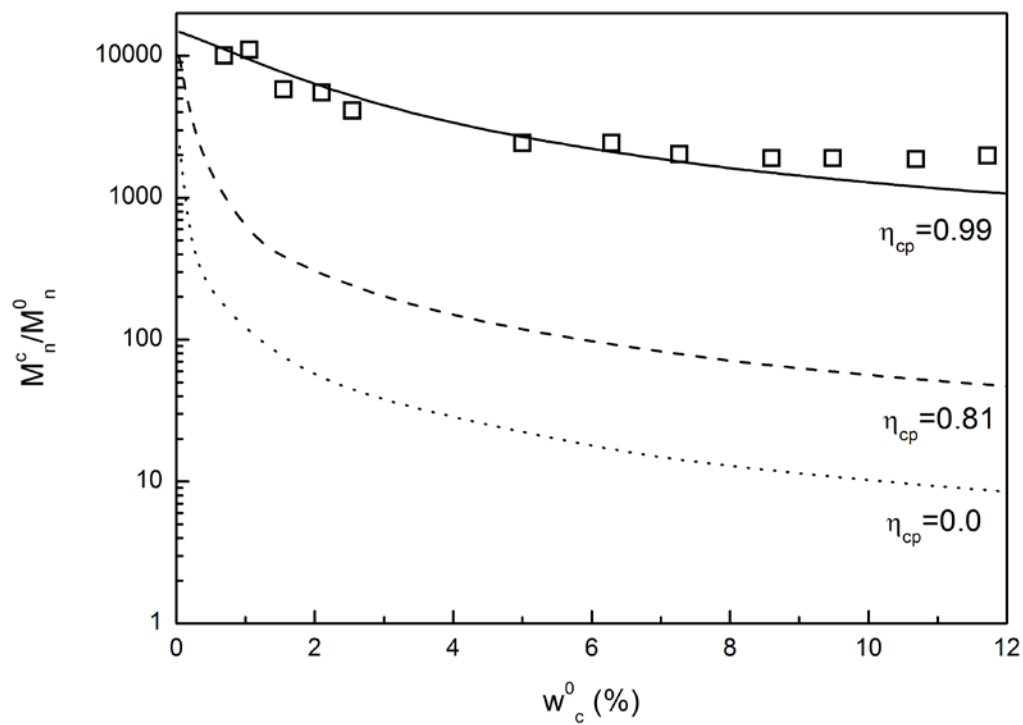


Figure 8. Repeating units between two consecutive crosslinks versus weight fraction of crosslinker for a given weight fraction of monomer mixture $w_t = 5\%$. Comparison between model predictions at different values of η_{cp} (lines) and experimental data from Okay²¹ (symbols).

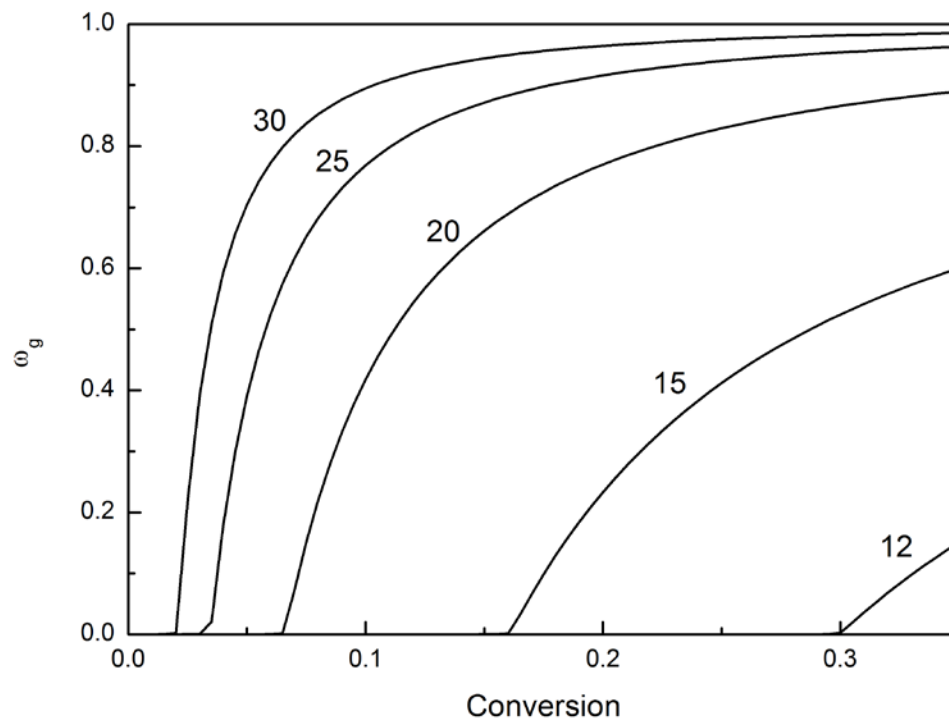


Figure 9 Gel fraction as a function of conversion for different values of w_t (numbers indicate weight percentages).

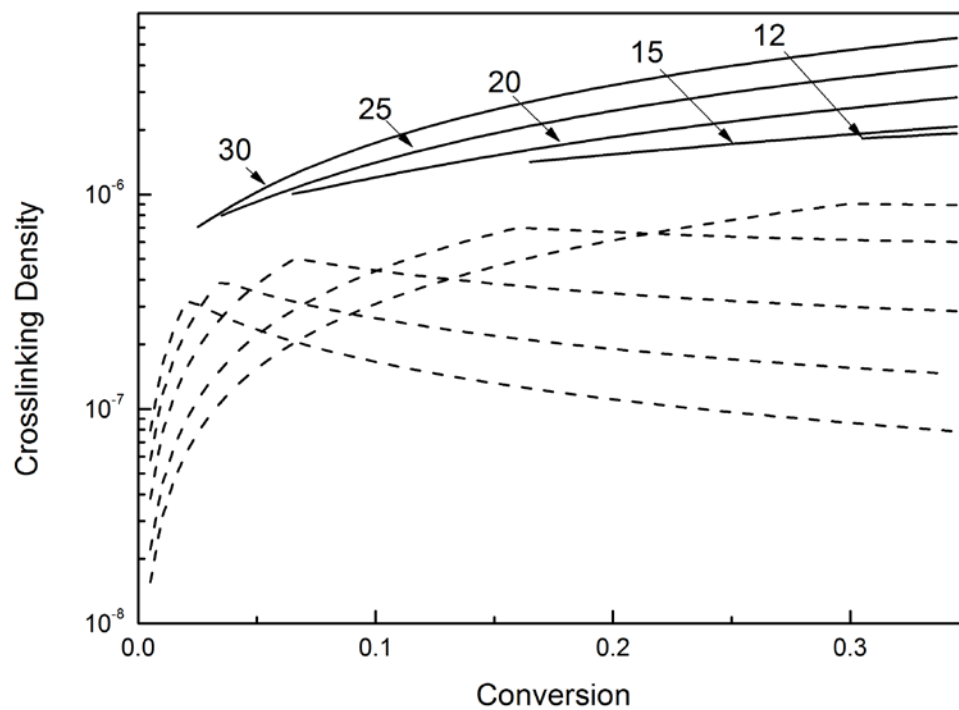


Figure 10 Crosslinking densities of sol (dashed lines) and gel (continuous lines) as a function of conversion for different values of w_i . (numbers indicate weight percentages).

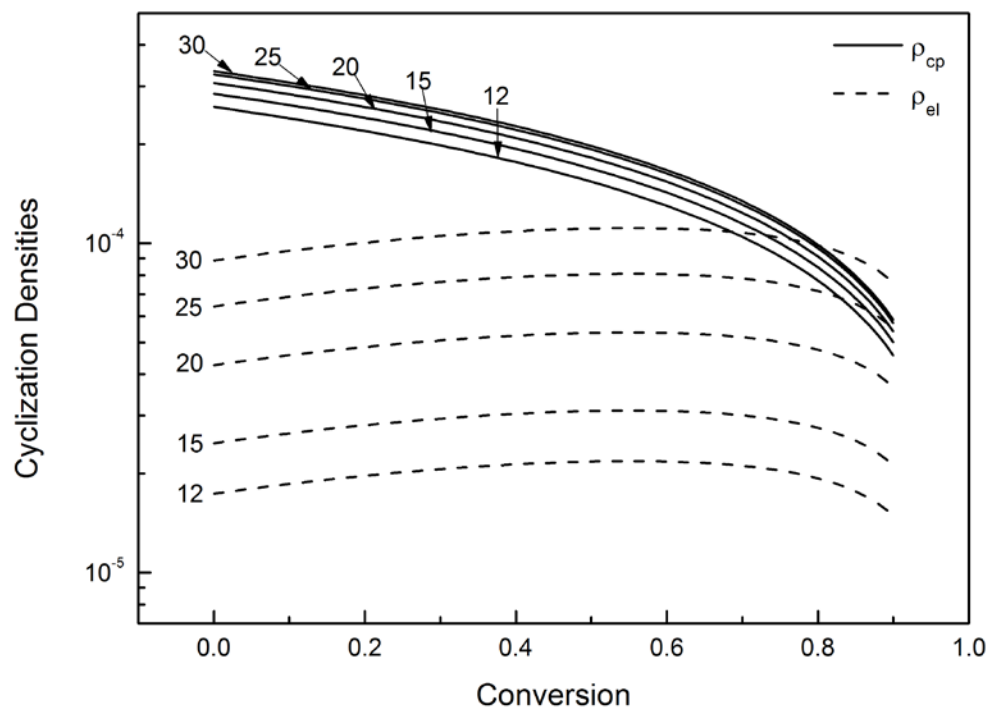


Figure 11 Primary (continuous lines) and elastic (dashed lines) crosslinking densities for different values of w_t . (numbers indicate weight percentages).