Features of crosslinking polymerization in laser stereolithography

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Abstract. The model of crosslinking polymerization in photopolymer for laser stereolithography has been proposed. The feature of this polymerization is that the initiation takes place by an irradiation with single pulse that should be enough to solidify the chosen parts of photopolymer. It is shown that despite of such initiation the polymerization passes the gel point due to the fast forming and crosslinking of polyradicals resulting in gel macromolecules. The influence of different factors (termination, trapping, crosslinking, cyclization) on position of the gel point is investigated. Branched level of macromolecules formed during polymerization is found to be mainly dependent on the rate of cyclization.

1. Introduction
The oldest additive manufacturing technology, laser stereolithography, still does not lose its importance and attracts users for application in industry, medicine, etc. [1]-[2]. As an advantage of this technology is that it can be utilized to manufacture highly complex and individually designed geometries of 3D objects. And also the technology exhibits high resolution and surface qualities.

Since the appearance of the technology in 1981 [3] a considerable progress has been made in developing new photopolymers allowing to create 3D objects with high physicochemical properties. In addition to polymeric objects, the fabrication of metallic and ceramic ones are possible by the technology [4]-[5]. Nevertheless the development of new photopolymers is a continuous challenging for laser stereolithography to improve and reach desirable properties of fabricated subjects for different applications [1]-[5]. To promote this development modeling and simulation becomes important to understand processes happening during solidification in photopolymers when a focused laser beam moves on the surface of this photopolymer.

Up to now in literature the kinetics of (co)polymerization in photopolymers has been described by simplified ways. The roughest approach uses the assumption that the solidification of a point in photopolymer is reached if the dose of radiation obtained by this point is above some border value [6]-[7]. This approach ignores completely details of (co)polymerization in photopolymer. Another approach considers the reactivity of any double bond in photopolymer as a unit of equal reactivity not discriminating whether this double bond belongs to the one of a non-reacted or reacted monomer [8]-[9]. Besides the solidification of a point in photopolymer is assumed to take place if conversion of double bonds at this point is reached a border value. Such consideration accounts for basic mechanisms of (co)polymerization including photoinitiation, propagation and termination of polymer chains. Nevertheless the approach does not take into account important features of crosslinking (co)polymerization in photopolymer used by laser stereolithography.
In this work first the crosslinking (co) polymerization in photopolymers has been considered as a subject of investigation. The aim of the work is to find out specific features of this (co)polymerization to facilitate the development of new photopolymers for laser stereolithography. Besides methacrylates and acrylates have been considered to be monomers for the photopolymers. These monomers are widely used for laser stereolithography and have a great potential for future application as a basis of new photopolymers with additives and fillers.

2. Model of crosslinking polymerization.
Three approaches – statistical, percolation and kinetic theories - are known to apply for description of the crosslinking polymerization [10]-[11]. Here in the following a kinetic approach has been used. Radical polymerization is a common mechanism for acrylic monomers; so the polymerization with this mechanism is a subject of the further investigation. For the simplicity the crosslinking polymerization of bifunctional methacrylate has been considered.

Initiation
\[ I \xrightarrow{k_t} 2jR_0^* \]  
\[ R_0^* + M \xrightarrow{2k_h} R_{1,l,j}^* \]  

Propagation
\[ R_{i,j,n}^* + M \xrightarrow{2k_h} R_{i+1,j,a+1}^* \]  

Termination
\[ R_0^* + R_0^* \xrightarrow{k_s} D_0 \]  
\[ R_{i,m,s}^* + R_{i,m-l,s}^* \xrightarrow{m_k} R_{i,m-l,s}^* \]  
\[ R_{i,j,n}^* + R_{i,j-n}^* \xrightarrow{j_{m-l,s}} R_{i+l,j-m+2,n+s}^* \]  
\[ R_{i,j,n}^* + R_{i+n,j-l,s}^* \xrightarrow{j_{m-l,s}} R_{i,j+n-l,s}^* + R_{i,m-l,s}^* \]  
\[ R_{i,j,n}^* \xrightarrow{j_{l,m,s}} R_{i,j-1,n}^* + R_{i,j-1,n}^* \]  

Crosslinking
\[ R_{i,j,n}^* + R_{i,j,n}^* \xrightarrow{(n+s+m+n)k} R_{i+l,j-m+n,s+1}^* + C \]  

Cyclization
\[ R_{i,j,n}^* \xrightarrow{k_c} R_{i,j,n+1}^* + C \]  

Chain transfer
\[ R_{i,j,n}^* + A \xrightarrow{k_t} R_{i,j,n}^* + R_0^* \]  

Inhibition
\[ R_{i,j,n}^* + Z \xrightarrow{j_{l,n}} R_{i,j,n}^* \]  

Trapping
\[ R_{i,j,n}^* \xrightarrow{k_a} R_{i,j-1,n}^* \]  

Scheme 1. Model of crosslinking polymerization in photopolymer consisting of initiator (I), bifunctional monomer (M) and inhibitor (I).

The developed model of crosslinking polymerization of photopolymer consisting from initiator (I), bifunctional monomer (M) and inhibitor (Z) is shown in scheme 1. The basic reactions of such polymerization – initiation, propagation, termination, chain transfer, crosslinking and cyclization – have been taken into account by the model. Laser radiation creates primary radicals \( R_0^* \) (S1); addition of monomer M (S2) to these radicals results in secondary growing radicals \( R_{i,j,n}^* \). For each polyradical indexes i, j and n indicate numbers of reacted monomers, radicals and pendant double bonds, respectively. The polyradicals participate in propagation reactions (S3). In addition to the termination for primary radicals ((S4), (S5)) the ones by disproportionation (S7) and combination (S6) for polyradicals have been considered. Also the termination inside \( R_{i,j,n}^* \) has been taken into account (S8). The main advantage of our work is that the reactions of crosslinking (S9) and cyclization (S10) have been taken considered. The term C in these reactions is a counter allowing to determine the number of pendant double bonds involved in reactions. The radical formed due to crosslinking is assumed to have the same reactivity towards all the reactions as the end radical because the both radicals formed from double
bonds show the same structure. Initiator, monomer or specially chosen substance could be considered as an agent in chain transfer reactions (S11). Inhibition is considered to take place by simple reaction (S12); the radicals formed due to this reaction are assumed not to be reactive. The radical trapping mechanism is also included (S13) in accordance with ref. [12]. It should be noted that the species $R^\cdot_{i,0,n}$ in scheme 1 are dead polymers as they contain no active radicals. Also if some reaction in the scheme results in a negative index this reaction should be omitted.

For crosslinking reaction (S9) it is taken into account that the coupling of two large macromolecules leads to a deactivation of some radicals simultaneously if these radicals becomes deeply inside the formed macromolecule. To take into account this trapping effect the crosslinking reaction is considered as

$$R^\cdot_{i,j,n} + R^\cdot_{l,m,n} \rightarrow R^\cdot_{i+l,0,n+s-1} + C \quad (1)$$

if $j+m>20$. Such consideration is also a consequence of the fact that the species having more than 20 radicals are not taken into account by the simulation.

The parameters used for simulation of crosslinking polymerization for bifunctional methacrylate at temperature 20 °C for laser stereolithography are presented in table 1. These parameters does not belong to polymerization of a specific monomer; nevertheless considering the polymerization of a virtual methacrylate we took into account the literature data concerning kinetic parameters for monomers of methacrylate family. For example the propagation rate coefficient ($k_p$) is chosen to be close to the mean value among the ones in [13]. The termination rate coefficient ($k_t$) is selected to ensure enough level of monomer-to-polymer conversion. The pendant double bond is expected to be less reactive than the free monomer double bond so that the crosslinking rate coefficient ($k_{cr}$) is chosen to be less than 400 L·mol$^{-1}$·s$^{-1}$. The methacrylates radicals are known to terminate mainly through disproportionation; that is way the mode of termination ($\delta = k_{td}/(k_{tc}+k_{td})$) is chosen. The cyclization rate coefficient ($k_{cyc}$) is selected to be a higher than the backbiting rate coefficient for acrylates [14] as it is expected that the pendant double bond is more reactive than the lateral bond of hydrogen to the chain. The coefficients of internal termination rate ($k_t$) and trapping ($k_{des}$) are chosen to be enough high but not so high to suppress the forming the gel point in the system. It should be pointed out that the molar mass of monomer is used to be 800 g·mol$^{-1}$. On the one hand this molar mass is too high for a methacrylate with two double bonds. At the same time this mass is chosen intentionally as in real photopolymers the monomers with close molar masses are used.

Table 1. Kinetic parameters for simulation of crosslinking polymerization at 20 °C for laser stereolithography

| Parameters                        | Values | Units     |
|-----------------------------------|--------|-----------|
| Propagation rate coefficient, $k_p$ | 400    | L·mol$^{-1}$·s$^{-1}$ |
| Termination rate coefficient, $k_t$ | 2000   | L·mol$^{-1}$·s$^{-1}$ |
| Termination rate coefficient, $k_{t0}$ | 2000   | L·mol$^{-1}$·s$^{-1}$ |
| Mode of termination, $\delta = k_{td}/k_t$ | 1      |           |
| Internal termination rate coefficient, $k_{t2}$ | 100    | s$^{-1}$  |
| Crosslinking rate coefficient, $k_{cr}$ | 200    | L·mol$^{-1}$·s$^{-1}$ |
| Cyclization rate coefficient, $k_{cyc}$ | 90     | s$^{-1}$  |
| Chain transfer rate coefficient, $k_{tr}$ | 0.1    | L·mol$^{-1}$·s$^{-1}$ |
| Inhibition rate coefficient, $k_z$ | $10^6$ | L·mol$^{-1}$·s$^{-1}$ |
| Trapping rate coefficient, $k_{des}$ | 5      | s$^{-1}$  |

To develop a program to utilize the model presented in scheme 1 with the parameters outlined in table 1 the program package PREDICI has been used. However to use this package one could use only one-dimensional massive with different chain lengths. To introduce the number of pendant double bonds
for macromolecule a counter C has been used for reactions (S9) and (S10); mean number of pendant double bonds for the macromolecule with chain length i could be estimated as i([M]₀-[M]-[C])/([M]₀-[M]). In addition one should consider independently the species having different number of radicals. Therefore according to scheme 1 the number of reactions used in the developed PREDICI program was 743 as the species containing up to 20 radicals have been considered.

3. Results and discussions
In the following in simulations the kinetic parameters are chosen to be equal to the values in table 1 except the ones that are varied as this is indicated in the text. For these kinetic parameters neither the chain-length nor conversion dependences are taken into account as the PREDICI allows to consider the polymerization up to only gel point. It is assumed that the initial concentration of inhibition (oxygen) in photopolymer is equal to 10⁻³ mol·L⁻¹ in accordance with ref.[15].

3.1. Crosslinking polymerization of polyradicals
For a chosen point of photopolymer the time of interaction with the moving focused beam is about 1 ms that is less than the time for addition monomer to radical (1/kₚ[M] ≈ 2 ms). So the production by initiation of primary radicals (of concentration = 4×10⁻³ mol·L⁻¹) could be considered to take place instantaneously. The important feature of the crosslinking polymerization is that such initiation by only one radiation pulse should result in solidification of preliminary chosen areas of the photopolymer; this necessity imposes restrictions for the kinetic parameters of the radical polymerization. For a chosen photopolymer ratio kₚ/kₜ should be enough low to ensure such solidification as this is shown by the time dependencies for monomer conversion in figure 1. For our photopolymer this ratio is chosen to be equal to 0.2. It is known that the crosslinking polymerization could only be considered in monoradical assumption if kₚ/kₜ < 10⁻³.[16] As kₚ/kₜ for our polymerization system is much higher than 10⁻³ the polymerization should take place through polyradicals. This is an important feature of the crosslinking polymerization in the stereolithography and that is why the polyradicals have been considered in scheme 1.

![Figure 1](image1.png)

**Figure 1.** Time dependences of monomer conversion for crosslinking polymerization at 20 °C for different kₜ. The kinetic parameters for calculations are taken from Table 1.

![Figure 2](image2.png)

**Figure 2.** Normalized molar mass distributions for dead macromolecules (D) and species Pj with j radicals at 0.05 s after the beginning of polymerization.
Figure 3. The time dependencies for dead macromolecules (D) and species $P_j$ with $j$ radicals.

Note that in figure 1 the conversion for $k_t = 2 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ has been presented only up to $t = 0.31$ s as this time is close to the gel point for our system. In the following some presented dependences will be also shown up to such restricted times as the used PREDICI allows to calculate these dependencies only up to the gel point as this indicated above.

The PREDICI allows to calculate molar mass distributions for the polyradicals as shown in figure 2. Also time dependencies for concentrations of the dead polymer and of the polyradicals could be calculated (figure 3). The behavior of such distributions and concentrations near the gel point is mostly interesting. As the gel point changes completely the kinetics of polymerization and determines the time of solidification of a part of photopolymer. Note that the increase of the concentrations of the species having high number of radicals could be observed near the gel point (figure 3c).

3.2. Polymerization degrees of crosslinking polymerization

The time dependences of weight degree of polymerization clearly demonstrate the presence of the gel point in the considered crosslinking polymerization despite of the specific initiation by one laser irradiation of this polymerization (figure 4). This gel point in time scale should be very close to the value for which weight degree of polymerization is equal to $10^7$ for dependence $M_w = M_w(t)$ going up sharply (figure 4). Note that the presence of the gel point has been obtained even for the case with termination taking place exclusively by disproportionation and introducing the intensive trapping of radicals according to (1). The reason of the appearance of the gel point is a rapid increase of species with higher number of radicals (figures 2 and 3).

Any factor that influences the concentration of radicals influences the position of the gel points as well (figure 4). If the consumption of radicals due to this factor is high no gel point could be observed (figures 1 and 4).

Figure 4. The time dependencies for number ($M_n$) and weight ($M_w$) degrees of polymerization for the different internal termination ($k_{\text{ter}}$) and trapping ($k_{\text{trap}}$) rate coefficients.
3.3. Branched level of crosslinking polymerization

Branching is an important feature of crosslinking polymerization as it influences highly the kinetics of this polymerization. This event is responsible for forming of insoluble gel even for monomer-to-polymer conversions below 10%. Also branching influences physicochemical properties of 3D objects created by laser stereolithography.

The branched level (a ratio of the branched number to the number of monomer addition) depends on the rate of crosslinking and cyclization according to reactions (S9) and (S10). Surprisingly the variation of the crosslinking rate coefficient results in minor change in the limit value of branching level as this is shown in figure 5a. At the same time the value of the crosslinking rate coefficient is a strong factor that influences the gel point as this is expected (figure 5b). For lower value of this coefficient (100 L⋅mol⁻¹⋅s⁻¹) the gel point is even absent.

A marked change of the branched level could be only reached by variation of the cyclization rate coefficient (figure 6a). So to reach a desired branched level in crosslinking polymerization one has to use a monomer providing the necessary rate of cyclization. At the same time a variation of the cyclization rate coefficient results in minor change in position of the gel point (figure 6b).

![Figure 5](image1)

**Figure 5.** The time dependencies for branching level (BL) and degrees of polymerization (Mn and Mw) for different values of the crosslinking rate coefficient (kcr).

![Figure 6](image2)

**Figure 6.** The time dependencies for branching level (BL) and degrees of polymerization (Mn and Mw) for different values of the cyclization rate coefficients (kcy).

4. Conclusions

Despite of the specific initiation by one laser irradiation the crosslinking polymerization in laser stereolithography takes place through the gel point. This result has been obtained even for the case with termination taking place exclusively by disproportionation and introducing intensive trapping of radicals according to (1). The fast forming and crosslinking of the species with high number of
radicals (polyradicals) is responsible for the creation of the gel macromolecules. Any factors influencing the concentration of radicals in a photopolymer could be a reason of lacking of the gel point in the system so that the possibility to use this photopolymer in laser stereolithography depends on these factors. In addition to reach the necessary level of branching the photopolymer should ensure enough rate of cyclization during polymerization as the crosslinking is found not to be able to give such level.

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