

Comparison of Network Structure Photopolymerized under UV-LED and High-Pressure Mercury Lamp with Different Photoinitiators

Kentaro Taki^{1*}, Takehiro Taguchi², Ryota Hayashi³, and Hiroshi Ito²

¹ *Chemical and Materials Engineering Course, School of Natural System, College of Science and Engineering, Kanazawa University,*

Kakumacho, Kanazawa, Ishikawa, 920-1192, Japan

² *Department of Polymer Science and Engineering,*

Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata, 992-8510, Japan

³ *Department of Natural System, Graduate School of Natural Science,*

Kanazawa University,

Kakumacho, Kanazawa, Ishikawa, 920-1192, Japan

**taki@se.kanazawa-u.ac.jp*

UV-curable resin of multifunctional monomers is believed to form a cross-linked network structure. However, the nature of this network is difficult to analyze. In this study, a kinetic approach was applied to compare the network structures of photopolymerized diurethane dimethacrylate cured by different light sources and photoinitiators. The conversion after UV irradiation was monitored to calculate the rate coefficients of propagation and termination (k_p and k_t , respectively) under varying irradiation times and at constant UV intensity and temperature. The values of k_p and k_t were compared for different UV light sources (a 365-nm peak UV-LED and a high-pressure mercury lamp) and different photoinitiators (1-hydroxycyclohexylphenylketone (HCAP) and 2,4,6-trimethylbenzoylphenyl phosphinate (TPO)). The results indicate that the network structure formed under different light sources with the same photoinitiator could be scaled, namely that the formed cross-linked network structures could be superimposed on top of each other by linear expansion or reduction. The reason is that the light sources only differ in the rate of photon delivery, while the photons are identical to each other in terms of chemical reactivity. In contrast, the network structures formed with different photoinitiators could not be scaled, since the photoinitiators differ in their quantum yield, kinetic constants, affinity, and molecular size. These factors could affect the network structure. Although the kinetic analysis in this study only provides very limited information about the network structure, we experimentally confirmed that the network structure depends on both the UV light source and photoinitiator.

Keywords: UV-LED, Mercury lamp, Cross-linked polymer

1. Introduction

Photopolymerization of multifunctional monomer forms intricate cross-linked networks. Such networks are difficult to analyze, because the combinatorial number of primary structures increases with the number of fully-polymerized multifunctional monomers. For example, the combinatorial number of 10 bifunctional monomers is 83,975 and that of 100 such monomers is 4×10^{58} . If one mole (6.02×10^{23}) of monomer is polymerized, the combinatorial number is astronomical. This is

the so-called the combinatorial explosion problem, and it indicates that the reproducibility of a specific primary structure is close to zero. In other words, it is very unlikely to produce the same network even if the polymerization condition is exactly controlled, although the produced polymers have the same macroscopic physical properties such as hardness and elasticity. The reason for the latter is that the physical properties are not determined by the primary structure, but the higher-order structure. These higher-order structures in UV-curable resin,

e.g., the size of cross-linked network and the number of dangling chains or loops are still unclear. It is essential to study the higher-order structure of UV-cured resin to control and improve their physical properties.

In typical non-solvent UV-curable resin, the polymerization of monomers is considered to occur in a solution with the monomer being the solvent. At the beginning, the primary radical reacts most easily with C=C bond in the monomer solution, because the diffusion of C=C bonds is not hindered in such diluted “polymer solution”. However, the diffusion of C=C bond to the radical becomes more difficult as the polymerization progresses, because the cross-linked network hinders the translation of C=C bonds [1]. The apparent rate constant of propagation drops with the formation of dense, cross-linked network. Thus, an analysis of the rate constants could possibly elucidate the cross-linked network structure.

Anseth et al. investigated the volume shrinkage, conversion, and kinetic chain length in the cross-linked network structure by means of kinetic measurement, matrix assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS), and gel permeation chromatography [2-4]. Their results indicated the existence of diffusion-controlled kinetics which is affected by the cross-linked network.

In our previous study, the effects of the monomer’s chain length on the rate constants of propagation and termination were investigated [5]. As mentioned above, the rate constants decrease with the gradual conversion of C=C bond, as the cross-linked network becomes dense and the diffusion rate of C=C bond is slowed down. The onset conversion of rate constant depression increases with increasing monomer chain length. The reason is that monomers with longer chains require more conversion to reach the diffusion-controlled regime, implying sparser cross-linked network.

UV-light emitting diode (LED) is a promising UV light source for industrial UV curing, because of the low energy consumption, small footprint, freedom from mercury, etc. Photopolymerization by UV or visible light is especially suitable for dental applications [6-13]. Recently, the group of Fouassier and Lalev e investigated novel photoinitiators for LED projector 3D printing [14-

18]. Moreover, Okamura et al. used different types and formulations of photoinitiators to compare the performance of deep UV-LED with the typical high- and medium-pressure mercury lamps and metal halide lamp [19]. They mainly focused on the sensitivity of the photoinitiator and conversion of C=C bond, and also briefly discussed the cross-linked structure of UV-cured monomers.

In this study, real-time Fourier transform infrared (FTIR) spectroscopy was employed for measuring the photopolymerization kinetics of diurethane dimethacrylate initiated by two different photoinitiators (Irgacure 184 and Irgacure TPO) and two different light sources (UV-LED at 365 nm and high-pressure mercury lamp). Dark polymerization analysis was employed to measure the rate constants for propagation and termination. A comparison of these rate constants elucidated the development of network structures formed using different combinations of photoinitiator and light source.

2. Theory

Under UV irradiation, the dissociation of the photoinitiator results in the continuous formation of its radicals, which readily react with the double bond to afford a primary radical. This primary radical then reacts with a monomer and forms a macro-radical. Thus, the monomer can react with radicals of the initiator, the primary radicals, or the macro-radicals. In the absence of the UV light, the photoinitiator would not dissociate. Therefore, no initiator radicals are produced, and the monomer is consumed by either the primary or macro-radicals. If the primary radical is a part of macro-radical, they should have the same kinetic constants, which are determined as the rate constant for propagation (k_p). This so-called dark polymerization method has been employed for determining k_p and k_t (the rate constant of termination), an approach that has been thoroughly reviewed by Andrzejewska [1] and applied in our previous studies [5,20,21].

If a bimolecular termination mechanism is assumed, two parameters (A and B) could be determined by fitting the conversion of experimental data as follows:

$$A = k_p / k_t \quad (1)$$

$$B = k_t [M_n]_0 \quad (2)$$

$$-\ln \frac{1-x_A(t)}{1-x_A(t_e)} = A \ln \{B(t-t_e) + 1\} \quad (3)$$

The polymerization rate is associated with that of the radical generation according to Eq. (4):

$$\frac{k_p}{\sqrt{k_t}}[M]_0(1-x_A)\sqrt{\phi I_0 \epsilon [PI]} = [M]_0 AB \quad (4)$$

The length of the dangling chain is related to the kinetic chain length [4]:

$$\nu = \frac{R_p}{R_t} = \frac{k_p[M][M_n^\bullet]}{k_t[M_n^\bullet]^2} \quad (5)$$

where k_t is the rate constant for binary termination, $[M]_0$ is the molar concentration of C=C double bonds for polymerization, $[M_n^\bullet]_0$ is the molar concentration of the macro-radical, x_A is the double bond conversion, and t_e is the time without UV-light. t is the time. η is the quantum yield, I_0 is the photo flux. ϵ is the molar absorption coefficient of the photoinitiator, and $[PI]$ is the photoinitiator concentration.

3. Experimental

3.1. Materials

The bifunctional monomer of diurethane dimethylmethacrylate (DUDM) was purchased from Sigma-Aldrich. The monomer contained 225 ± 25 ppm of topanol as inhibitor. The photoinitiators, namely Irgacure 184[®] (HCAP) and Irgacure TPO (TPO), were supplied by BASF (Germany). All reagents were used without further purification. The weight ratios of the monomer to HCAP and TPO were 99:1 and 97.7:2.3, respectively, in order to obtain the same molar ratio. The monomer and photoinitiator were mixed for 20 min and stored in a refrigerator at 5 °C. The absorbance spectra of the photoinitiators were measured with a UV/Vis spectrometer (V-550, JASCO).

3.2. UV lamps

Two UV light sources were used: a high-pressure mercury lamp (Omnicure[™] S2000, EXFO Co., Canada) through a liquid light guide, and a UV-LED lamp (LX400, EXFO Co., Canada). The UV intensity was measured by a photometer (UIT-150, USHIO, Japan) at 365 nm. The spectra of the light sources were measured with a mini-spectrometer (C11007MA, Hamamatsu Photonics, Japan). Typical spectra of the light sources and the absorbance of photoinitiators are shown in Fig. 1.

3.3. Real-time FTIR measurement

The measurement technique was same as in a previous study [21]. Briefly, two 5 mm × 5 mm × 0.5^t mm KBr plates (JASCO, Japan) were used. A

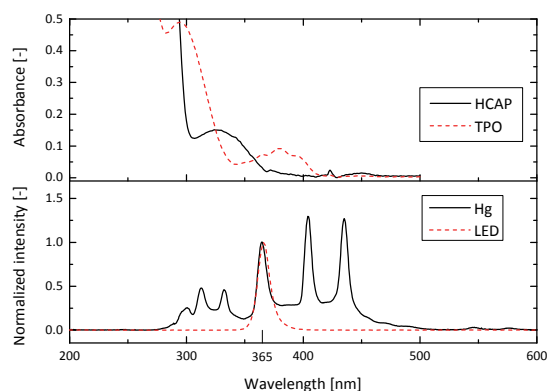


Fig. 1. Top: absorbance spectra of HCAP and TPO. Bottom: typical spectra of the high-pressure mercury lamp (Hg) and the UV-LED lamp.

shim ring with a thickness of 10 μm, inner diameter of 3 mm, and outer diameter of 5 mm was used to maintain a constant solution thickness for all measurements. The sample plate was prepared as follows. First, the shim ring was placed on one KBr plate, and a drop of the monomer solution was placed at the center of the shim ring. Next, the other KBr plate was placed over the shim ring.

The assembled sample plate was placed on a stage, which was maintained at 47 °C, of the optical bench of a real-time FTIR (VERTEX 70, Bruker-Optics, Germany) system. The beam from the FTIR beam splitter was transmitted to the normal direction of the sample plate. Simultaneously, the sample plate was irradiated by UV light from an incident angle of 45°. When using the high-pressure mercury lamp, the UV light was transmitted through a liquid light guide. The UV intensity was measured by a photometer (UIT-150, USHIO, Japan). For better reproducibility, the UV intensity was adjusted to 10 ± 0.1 mW/cm² by changing the position of the liquid light guide and the iris of the lamp. A photodiode (GaAsP, G5842, Hamamatsu Photonics, Japan) was used to check whether the UV light was on or off.

The conversion is typically measured as follows. (1) The UV intensity is adjusted using a UV meter. (2) The sample plate is placed on the temperature-controlled stage. (3) Real-time FTIR measurement is carried out under UV exposure. (4) UV light is switched off after a pre-determined time. (5) Real-time FTIR measurement was continued for another 60 s to monitor dark polymerization. The absorbance peak height at 812 cm⁻¹ was utilized for calculating the conversion, and the wavenumber resolution was 8 cm⁻¹. Thirty-three spectra were

recorded every second.

Tables 1 and 2 summarize the parameters used for the measurement and calculation of the kinetic constants.

Table 1. Parameters of experimental condition

Parameter	Value
UV intensity, E_0	10 mW/cm ²
Photon flux, I_0	3.05×10^{-4} E/m ² /s
Temperature, T	320.15 K (47°C)
Molar concentration of the double bond, $[M]_0$ [mol/m ³]	4.12 mol/L

Table 2. Parameters of photoinitiators

	HCAP		TPO	
	Irgacure 184	Irgacure TPO	Irgacure 184	Irgacure TPO
Molar absorption coefficient, ϵ [m ³ /mol/m]	17.17	50.42		
Molar concentration, $[PI]$ [mol/m ³]	53.8	53.8		
Quantum yield, ϕ [-]*	0.8	0.7		

*[22]

4. Results

k_p was measured with the dark polymerization method described above for two UV light sources and two photoinitiators. Figure 2 shows the effect of light source on k_p . The value of k_p increased with increasing conversion of the methacrylate group, till the conversion is close to 0.2. Then it drops with further conversion. As reported in our previous study [20], the dissolved oxygen from air in the UV-curable resin sample inhibited the propagation reaction and reduced the rate constant. When the conversion was over 0.2, the rate constant decreased as the cross-linked network was formed and its density increased.

When using HCAP as the photoinitiator, the high-pressure mercury lamp (Hg-HCAP) shows higher k_p than UV-LED (LED-HCAP) in the conversion range of 0.2–0.7. The slope of k_p vs. conversion in the range of 0.4 to 0.7 is similar for Hg-HCAP and LED-HCAP. In Fig. 3, when using TPO as the photoinitiator, the k_p value of high-pressure mercury lamp (Hg-TPO) is higher than that of UV-LED (LED-TPO) from 0.5 to 0.7. Again, the slope of Hg-TPO is close to that of LED-TPO in the range of 0.5–0.7.

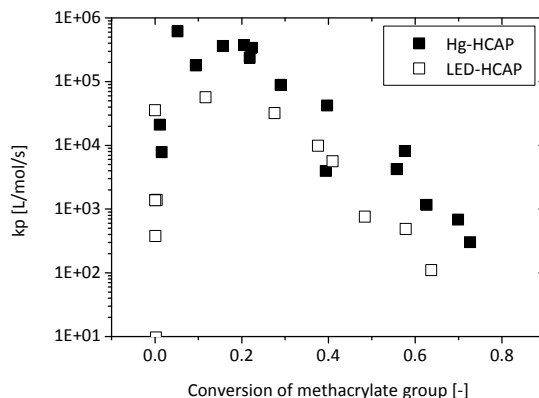


Fig. 2. Effect of UV light source on k_p when using HCAP. Conditions: 10 mW/cm², 47 °C.

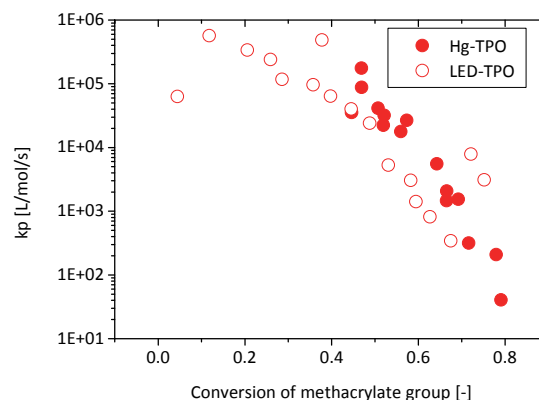


Fig. 3. Effect of UV light source on k_p when using TPO. Conditions: 10 mW/cm², 47 °C.

The data in Figs. 2 and 3 can be rearranged to illustrate the effects of the photoinitiator with the same UV light source. In Fig. 4, k_p is higher for Hg-TPO than for Hg-HCAP in the conversion range of 0.4–0.6, while their values are similar between 0.6–0.7. The slope of TPO is higher than that of HCAP. A similar trend could be observed for the UV-LED light source, as shown in Fig. 5. The slope of LED-TPO is lower than that of LED-HCAP in the range from 0.3 to 0.5.

The rate coefficient of binary termination was measured with the aid of the dark polymerization method. The four sets of results are plotted in Fig. 6. The trend of k_t is close to that of k_p .

The kinetic chain length was calculated from Eq. (5) and shown in Fig. 7. When they are compared at the same conversion above 0.4, the kinetic chain length increased with the order of LED-HCAP, LED-TPO, Hg-HCAP, and Hg-TPO at the conversion of 0.6.

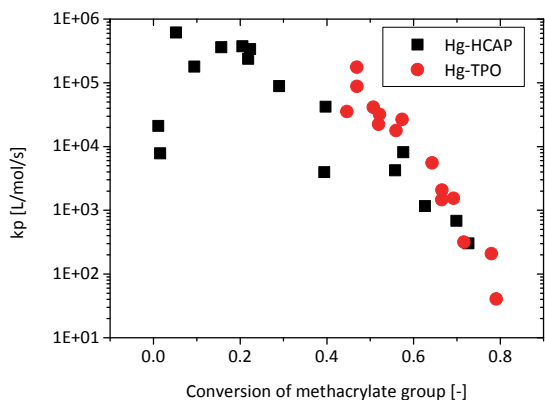


Fig. 4. Effect of photoinitiator on k_p under high-pressure mercury lamp. Conditions: 10 mW/cm², 47 °C.

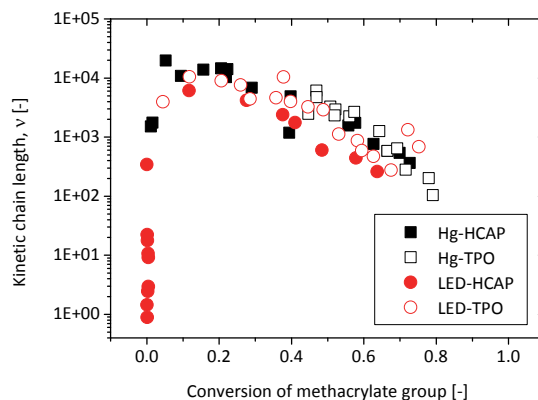


Fig. 7. Kinetic chain length calculated from the rate coefficients.

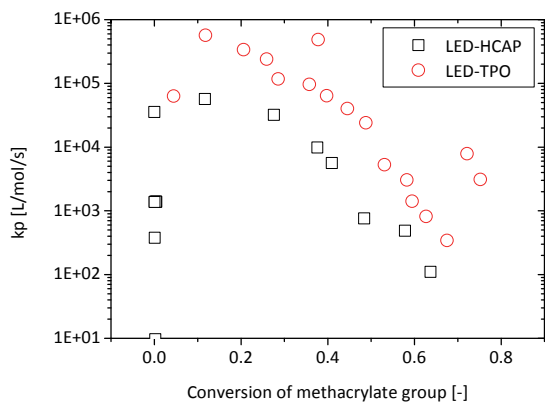


Fig. 5. Effect of photoinitiator on k_p under UV-LED. Conditions: 10 mW/cm² and 47 °C.

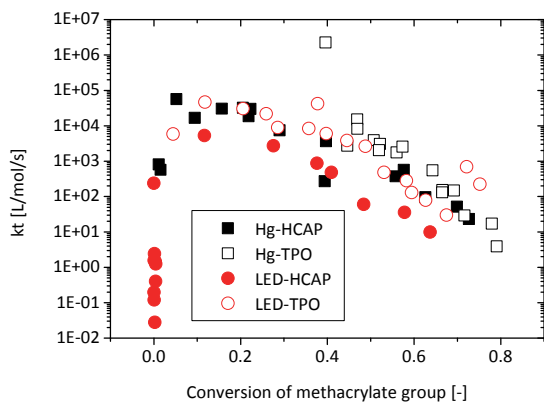


Fig. 6. Rate coefficients of binary termination for HCAP and TPO under high-pressure mercury lamp and UV-LED.

5. Discussion

In summary, we found that the plots of different light sources and the same photoinitiator (namely, between Hg-HCAP and LED-HCAP, and between Hg-TPO and LED-TPO) could be superimposed, since the two sets of data show similar slopes, as shown in Figs. 1 and 2.

The value of k_p , which is calculated from Eqs. (1)–(4), is affected by the molar absorption coefficient of the photoinitiator. A larger molar absorption coefficient leads to a lower calculated k_p . In this study, the molar absorption coefficients measured at 365 nm could be used to calculate k_p for the UV-LED lamp, which is unimodal and has its peak wavelength at 365 (Fig. 1). On the other hand, the spectrum of high-pressure mercury lamp is multimodal and shows three peaks below 365 nm. Photons at these wavelengths could also dissociate the photoinitiators, which would induce the subsequent polymerization. In this case, more photons react with the photoinitiator than that estimated by the molar absorption coefficient at 365 nm. Therefore, it is reasonable to shift the k_p values of Hg-HCAP and Hg-TPO downward to elucidate the effects of photoinitiators on k_p . Specifically, the plots of Hg-HCAP and Hg-TPO were shifted downwards by multiplying the shift factors of 0.1 and 0.25, respectively. The shift factor was determined by minimizing the difference in k_p between the two lamps. As shown in Figure 8, after shifting the results for the high-pressure mercury lamp, the data for Hg-HCAP and LED-HCAP overlap with each other well, and so do those of Hg-TPO and LED-TPO.

The slope in Figure 8 in the conversion range of 0.2–0.8 changes for the two photoinitiators. The k_p of HCAP drops almost linearly in this range, while

that of TPO decreases slowly from 0.2 to 0.5 with a similar slope to HCAP, and then increases sharply after 0.5. As explained earlier, the cross-linked network structure could interfere with the diffusion of C=C bond and therefore reduce k_p . This hypothesis suggests that in Figure 8, the cross-linked network for TPO becomes significantly denser at the conversion of 0.5, while this does not occur for the network formed with HCAP.

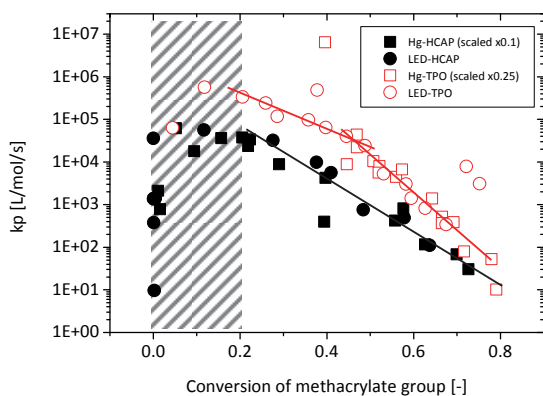


Fig. 8. Scaling of rate coefficient of propagation.

Figure 9 shows the kinetic chain length in which data for the mercury lamp is scaled by a factor of 0.4. The kinetic chain length is influenced by the oxygen inhibition in the gray-hatched area. Similar to the results of k_p , the scaled plot of kinetic chain lengths shows no difference between the light sources, and the difference between the photoinitiators becomes prominent in the conversion range of 0.2 to 0.8.

From the above discussions, the k_p and kinetic chain length for the same photoinitiator but different light sources become identical by using a simple scaling factor. This indicates that the network structures formed by different light sources could also be scaled. Although the number of cross-linked points depends on the light source, the network structures are similar, and one can be expanded/reduced to match the other by a simple scaling relationship.

On the other hand, the two different photoinitiators in this study formed different network structures that cannot be matched by simple scaling. Specifically, TPO formed sparse cross-linked network up to the conversion of 0.5, and then the network became dense with increasing conversion. In contrast, the network structure formed with HCAP became denser at an even rate with conversion without sudden changes.

Although the kinetic analysis in this study only

provides very limited information about the network structure, we found that the network structure depends on both the UV light source and photoinitiator. With regard to the light source, the difference in network structure could be scaled, which is not the case for the different photoinitiators. This is because the UV light sources only differ in the rate of photon delivery, while the photons are identical to each other in terms of chemical reactivity. In contrast, the photoinitiators differ in their quantum yield, kinetic constants, affinity, and the size of molecule. These factors could affect the network structure.

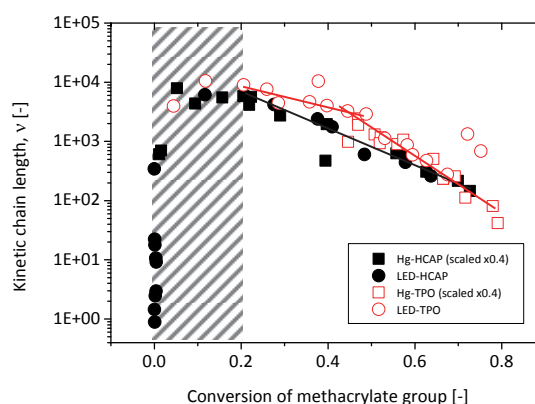


Fig. 9. Effects of UV light source and photoinitiator on kinetic chain length.

6. Conclusion

The rate constants of k_p and k_t in the photopolymerization of multifunctional monomers were measured and compared for two different UV light sources (high-pressure mercury lamp and UV-LED) as well as different photoinitiators (HCAP and TPO). The results indicate that the network structure formed by different UV light sources with the same photoinitiator could be scaled. However, this is not true for network structures formed with different photoinitiators. The reason is that, while the light sources deliver photons with the same reactivity at different rates, the two photoinitiators display different chemical properties, such as reactivity, affinity, and molecular size.

Acknowledgement

This study was supported by the Grant-In-Aid of Japanese government for Challenging Exploratory Research (16K14469). We would like to thank Editage (www.editage.jp) for providing English language editing service.

References

1. E. Andrzejewska, *Prog. Polym. Sci.*, **26** (2001) 605.
2. K. S. Anseth, C.N. Bowman, and N. A. Peppas, *J. Polym. Sci. Pol. Chem.*, **32** (1994) 139.
3. A. K. Burkoth and K. S. Anseth, *Macromolecules*, **32** (1999) 1438.
4. J. A. Burdick, T. M. Lovestead, and K. S. Anseth, *Biomacromolecules*, **4** (2003) 149.
5. K. Taki, T. Taguchi, R. Hayashi, and H. Ito, *J. Photopolym. Sci. Tech.*, **29** (2016) 133.
6. F. Stahl, S. H. Ashworth, K. D. Jandt, and R. W. Mills, *Biomaterials*, **21** (2000) 1379.
7. D. L. Leonard, D. G. Charlton, H. W. Roberts, and M. E. Cohen, *J. Esthet. Restor. Dent.*, **14** (2002) 286.
8. A. Uhl, R. W. Mills, and K. D. Jandt, *Biomaterials*, **24** (2003) 1787.
9. M. G. Neumann, W. G. Miranda Jr, C. C. Schmitt, F. A. Rueggeberg, and I. C. Correa, *J. Dent.*, **33** (2005) 525.
10. M. G. Neumann, C. C. Schmitt, G. C. Ferreira, and I. C. Corrêa, *Dent. Mater.*, **22** (2006) 576.
11. N. Ilie and R. Hickel, *Dent. Mater.*, **27** (2011) 348.
12. D. C. R. S. de Oliveira, E. J. Souza-Junior, A. Dobson, A. R. C. Correr, W. C. Brandt, and M. A. C. Sinhoreti, *J. Appl. Oral Sci.*, **24** (2016) 555.
13. M. V. L. Bertolo, R. C. M. Moraes, C. Pfeifer, V. E. Salgado, A. R. C. Correr, and L. F. J. Schneider, *Braz. Dent. J.*, **28** (2017) 35.
14. C. Dietlin, S. Schweizer, P. Xiao, J. Zhang, F. Morlet-Savary, B. Graff, J. P. Fouassier, and J. Lalevée, *Polym. Chem.*, **6** (2015) 3895.
15. J. Zhang, F. Dumur, P. Xiao, B. Graff, D. Bardelang, D. Gigmes, J. P. Fouassier, and J. Lalevée, *Macromolecules*, **48** (2015) 2054.
16. J. Zhang, P. Xiao, F. Dumur, C. Guo, W. Hong, Y. Li, D. Gigmes, B. Graff, J. P. Fouassier, and J. Lalevée, *Macromol. Chem. Phys.*, **217** (2016) 2145.
17. A. Al Mousawi, A. Kermagoret, D. L. Versace, J. Toufaily, T. Hamieh, B. Graff, F. Dumur, D. Gigmes, J. P. Fouassier, and J. Lalevée, *Polym. Chem.*, **8** (2017) 568.
18. A. Al Mousawi, C. Poriel, F. Dumur, J. Toufaily, T. Hamieh, J. P. Fouassier, and J. Lalevée, *Macromolecules*, **50** (2017) 746.
19. H. Okamura, S. Niizeki, T. Ochi, and A. Matsumoto, *J. Photopolym. Sci. Technol.*, **29** (2016) 99.
20. K. Taki, Y. Watanabe, H. Ito, and M. Ohshima, *Macromolecules*, **47** (2014) 1906.
21. K. Taki, Y. Watanabe, T. Tanabe, H. Ito, and M. Ohshima, *Chem. Eng. Sci.*, **158** (2017) 569.
22. J.-P. Fouassier and J. Laevee, "Photoinitiators for Polymer Synthesis: Scope, Reactivity, and Efficiency", Wiley-VCH Verlag & Co. KGaA, Boschstr, Weinheim, 2012.