Enhancement of Dark Polymerization by Oxygen Quenching during Network Formation in Ultraviolet-Light-Induced Radical Polymerization of Multifunctional Monomers and Reactive Polymer

Kentaro Taki*, Ryota Hayashi, Takatoshi Taniguchi, and Asuka Tsuneishi

1 School of Mechanical Engineering, 2 Graduate School of Natural Science, 3 School of Natural System, Kanazawa University, Kakuma Machi, Kanazawa, Ishikawa, 920-1192, Japan 4 Science and Innovation Center, Mitsubishi Chemical Corporation, 1000, Kamoshida-cho, Aoba-ku, Yokohama-shi, Kanagawa 227-8502, Japan
*taki@se.kanazawa-u.ac.jp

This study investigated the impact of oxygen quenching on dark polymerization by changing the atmosphere from nitrogen to air after stopping UV light irradiation. Real-time FT-IR measurements showed that C=C bond conversions of multifunctional monomers (diurethane dimethacrylate, dipentaerythritol penta-/hexa-acrylate) and a reactive polymer in which the functional group was acrylate were 0.01–0.04, greater than that in an environment of continuous nitrogen purging, when the UV irradiation dose larger than 3 mJ/cm² with a photoinitiator 1-[4-(phenylthio)phenyl]-1,2-octanedione 2-(O-benzoyloxime) (OXE01). Kinetic analysis of the dark polymerization elucidated that it was promoted when the polymerization and termination reaction rates were controlled by the diffusion of the C=C bond groups. Exposure to oxygen caused a portion of dangling radicals to be quenched, stopping the reaction and forming a dense network structure. The remaining dangling radicals could continue the polymerization, and more C=C bonds were converted than that in the continuing nitrogen atmosphere. This effect was not observed on using another photoinitiator, 1-hydroxycyclohexyl phenyl ketone (HCK), and diurethane dimethacrylate. The promotion of dark polymerization thus depends on the photoinitiator. Promotion of dark polymerization was observed in the case of OXE01 as it is less susceptible to the radical quenching of oxygen.

Keywords: Photopolymerization, Network, Oxygen inhibition

1. Introduction

Oxygen is a well-known inhibitor for radical photopolymerization. In photopolymerization via UV curing, oxygen inhibition results in incomplete curing, leaving behind unreacted layers or tackiness on the surface of the UV-curable resin. Therefore, preventing oxygen inhibition is an important challenge in the UV-curing industry. There have been many studies and industrial developments to prevent oxygen inhibition, by the use of photoinitiators, monomers, additives, gas atmosphere, and equipment [1,2]. In oxygen inhibition, oxygen attacks various types of radicals, such as initiators and the primary, macro, and dangling radicals, to form peroxides at their tip (Fig. 1).

This attack by oxygen on the dangling radical leaves behind the peroxide of the dangling chain (i.e., dead dangling chain). The peroxide does not react as well with C=C bonds as they do with each other; therefore, the polymerization of the radical ceases and binary termination of the two dangling radicals do not occur [3,4]. The objective of this study is to analyze the changes in the network
structure and C=C bond conversion due to oxygen attack on dangling radicals that are connected to a network structure.

Fig. 1. Radicals, C=C bond group, and oxygen in the network structure during the photopolymerization of UV-curing resin. This study makes a distinction between the macro radical and the dangling radial. The macro radical has a degree of polymerization greater than two and can freely move, while the dangling radical is the macro radical attached to the network structure.

The network structure of UV-curable resins formed without oxygen quenching has been studied extensively over the past two decades. Kinetic measurements and mathematical modelling of photopolymerization are powerful methods to investigate the network structure. The kinetic gelation model was used to predict the complex network structures that arise in the high-crosslinking regime in the case of homopolymerizations and copolymerizations of multifunctional monomers [5,6]. The kinetic constants, kinetic chain length, and their dependence on the termination reaction rate constants reflect the network structure [7-13]. Stochastic modeling based on the Monte Carlo method of network formation was applied to draw a realistic network structure. Further, a kinetic gelation model that simulates free radical network polymerization on a lattice was developed with a stochastic kinetic approach to enable real-time calculation, in order to assess how the initiation rate and primary cyclization affect the structural inhomogeneity and the overall kinetics of polymerization of multifunctional monomers [14,15]. However, despite extensive studies on the network structure, the impact of oxygen inhibition on the kinetic constant and network structure has not been investigated in depth [16].

UV curing is the bulk photopolymerization of multifunctional monomers, where the polymerization rate decreases with the increase in density of the network structure [17-20]. The network structure is formed by the binary termination reaction of two dangling radicals, which creates a C-C covalent bond. Successive binary termination reactions make the network structure dense, which hinders the diffusion of radicals and C=C bond groups like trapping fish in a net. As a result, the conversion of the C=C bond cannot approach 100%.

If the binary termination reaction that creates the dense network structure is suppressed during propagation, then the conversion of the C=C bond would be increased as the hindrance by the network structure lessens. Hence, the challenge is to suppress binary termination while continuing the propagation. This study focuses on the oxygen quenching of the dangling radical. Generally, when a dangling radical is quenched by oxygen, both termination and propagation reactions stop, so an increase in the C=C bond conversion cannot be expected. However, if the sample is exposed to oxygen after the network structure has partially developed, the network structure retards the diffusion rate of oxygen and increases the oxygen concentration in the sample. Then, the oxygen should attack a part of the dangling radicals and suppress network formation, while the remaining dangling radicals can undergo polymerization.

Using real-time FT-IR measurements, this preliminary study investigated the impact of oxygen quenching on the conversion of the C=C bond by dark polymerization during network formation. The network structure was formed by the UV-induced photopolymerization of multifunctional monomers or a reactive polymer in nitrogen atmosphere for a given irradiation duration. The impact of oxygen quenching on the network was then compared in terms of the network structure formed subsequently under air exposure and under continuous nitrogen purging.

2. Materials and method
2.1. Materials
The following multifunctional monomers, a monofunctional monomer, and polymer were used: dipentaerythritol penta-/hexa-acrylate (DPHA, contains ≤650 ppm MEHQ as inhibitor, 407283, Sigma-Aldrich), a reactive polymer containing acrylate side chains (RP, Mitsubishi Chemical, Japan), diurethane dimethacrylate (DUDM, containing 225 ppm±25 ppm topanol as inhibitor, purity≥97%, 436909, Aldrich), and mono(2-acryloyloxyethyl)succinate (MONO, stabilized with MEHQ, M1824, Tokyo Chemical Industry, Japan). The concentration of the
functional groups and viscosity are listed in Table 1. The photoinitiators used were 1-[4-(phenylthio)phenyl]-1,2-octanedione (OXE01, BASF) and 1-hydroxycyclohexyl phenyl ketone (HCK, Irgacure 184, BASF). The solvent was propylene glycol 1-monomethyl ether 2-acetate (PGMEA). Except RP, all materials were available commercially. The chemical structure of RP is shown in Fig. 2 and has been reported in other studies [21]. The weight-average molecular weight and acid value of RP were 9,000 and 30 mg KOH/g, respectively.

![Chemical structure of RP](image)

Fig. 2. Structure of reactive polymer (RP).

2.2. Sample preparation

A 2 cm × 2 cm piece was cut from the silicon wafer using a diamond cutter, and then soaked in the piranha solution for 40 min followed by rinsing with distilled water. The piece was then placed on a spin coater and rinsed with isopropyl alcohol. The sample solution was cast on the wafer according to the conditions presented in Table 1 using a spin coater (1H-D7, MIKASA, Japan). In order to dry the sample on the silicon wafer, it was pre-baked on a hot-plate (HP-2SA, AZ-One, Japan) at 100 °C for the durations shown in Table 1. The pre-baked sample thickness was measured using the spectral interference method (F20, Filmetrix, Japan), and the typical value obtained was 2.0–2.3 μm. The sample preparation and FT-IR measurements were conducted in a yellow room to avoid any stray UV light.

2.3. UV light source

Real-time FT-IR spectroscopy analysis was carried out using a UV light source (OmniCure S2000 High-Pressure 200-Watt Mercury-Vapor Short Arc lamp, EXFO, Mississauga, Ontario, Canada) equipped with a liquid light guide (ϕ 5 mm × 1500 mm, P/N 805-00028, EXFO, Mississauga, Ontario, Canada) to irradiate the monomer/initiator mixtures. The incident light has a maximum intensity of 365 nm, which was monitored using a UV radiometer (UIT-150, USHIO, Japan) prior to each characterization.

2.4. Real-time FT-IR measurement

The measurement system was developed in our previous study [16]. It was slightly modified to control the atmosphere around the sample. Real-time FT-IR spectroscopy (VERTEX 70, Bruker Optics, Germany) was used to monitor the polymerization kinetics. A schematic of the optical bench is illustrated in Fig. 3. A horizontal-transmission accessory (HTA) was used to ensure uniform illumination across the sample. The system was able to capture spectra at various stages of polymerization, allowing for a detailed analysis of the reaction kinetics.

### Table 1. Physical properties of monomers and reactive polymer.

| Abbreviation | DPHA | RP | DUDM | MONO |
|--------------|------|----|------|------|
| Polymerizable functional group | Acrylate | Acrylate | Methacrylate | Acrylate |
| Analyzed wavenumber of C=C bond [cm⁻¹] | 809.95 | 809.95 | 815.74 | 809.95 |
| Number of functional groups | 6 | ca. 35 | 2 | 1 |
| Molar concentration of functional group [mol/L] | 11.7 | 3.76 | 4.52 | 5.13 |
| Molecular weight [g/mol] | 578.55 | ca. 9,000 | 470.56 | 216.29 |
| Viscosity at 25 °C [mPa·s] | 6,600 | - | 10000 | 180 |
| Monomer or polymer [wt%] | 44.6 | 34.7 | 44.6 | 49.70 |
| Photoinitiator [wt%] | 0.9 | 0.7 | 0.9 | 0.497 |
| Solvent [wt%] | 54.5 | 64.4 | 54.5 | 49.70 |
| Solid content [wt%] | 98.0 | 98.0 | 98.0 | 99.0 |
| Spin-cast speed [rpm] | 1700 | 3400 | 1400 | 3400 |
| Casting time [s] | 60 | 60 | 30 | 15 |
| Pre-baking time [min] | 5 | 6 | 5 | 1 |
| Pre-baking temperature [°C] | 100 | 100 | 100 | 100 |
| UV intensity at 365 nm [mW/cm²] | 10 | 10 | 1 | 0.1 |
designed to enable horizontal mounting for FT-IR measurements. A mercury cadmium telluride (MCT) detector and KBr-coated beam splitter combination were used in conjunction with the rapid-scan option of the spectrometer to obtain a temporal resolution (33 ms) sufficient for monitoring the photopolymerization. The UV light source was located 3 cm above the sample. The sample stage was maintained at 30 °C using a temperature-control device, which was designed and constructed for use with a ceramic heater (Systems Engineering, Tokyo, Japan) in conjunction with the horizontal-transmission accessory. The sample was placed on the sample stage, and its horizontal position was adjusted to obtain the pre-determined absorbance for each sample. After closing the sample chamber cover, the sample chamber was purged with nitrogen flow (purity: 99.999 %, 5.0 L/min) for at least 4 min. The oxygen concentration was monitored by using an oxygen meter (Galvanic cell type, JKO-O2 ver. III, JIKO, Japan). In the case where the sample chamber cover was closed and nitrogen gas was flushed therein, the oxygen concentration was kept less than 0.1 vol%, which was the minimum detection limit for the oxygen meter. When the sample chamber cover was removed, the oxygen concentration gradually returned to the atmospheric concentration, i.e., 21%. The change in the atmosphere from the purge atmosphere to air will be termed “purge-to-open” operation hereafter. The measurement under air and nitrogen atmospheres are termed “open” and “purge”, respectively.

To investigate the impact of oxygen quenching on C=C bond conversion, the conversions of dark polymerization in the purge-to-open and purge operations were compared at 50 s after stopping irradiation. For accuracy in comparison, the conversions must agree within ±0.01 upon stoppage of irradiation. In the purge-to-open and purge operations, the sample was exposed to nitrogen purge atmosphere during irradiation. Ideally, the conversions should agree upon stoppage of irradiation. However, if the samples had slightly different initial thickness values, their conversions upon stoppage of irradiation would also differ. To ensure the same initial thickness, the initial absorbance of the C=C bond (809 or 815 cm⁻¹ depending on the acryl or methacryl group) was adjusted to a pre-determined value by carefully moving the sample horizontally with a tweezer. With the adjustment, the typical absorbance difference was less than 0.005 when irradiation was stopped.

The UV intensity was adjusted to the desired value (± 2%) by changing the iris and distance from the tip of the light guide and sample before setting the sample on the stage. The ON-OFF-timing of the UV light was precisely monitored and synchronized by a UV sensor in front of the sample. Each measured spectrum was processed using the peak deconvolution software developed in our laboratory.

![Fig. 3. Optical bench for the real-time FT-IR measurement.](image-url)
polymerization rate $R_p$ is expressed as shown in Eq. (3):

$$R_p = -\frac{k_p}{\sqrt{k_t}}[M]_0(\phi I_0 c[PI])^{0.5}$$  \hspace{1cm} (3)

where $k_p$ and $k_t$ are the kinetic constants of propagation and termination, respectively. $[M]_0$ is the molar concentration of the C=C bond when irradiation stopped, $\phi$ is the quantum yield, $I_0$ is the UV intensity, $c$ is the molar absorption coefficient, and $[PI]$ is the molar concentration of the photoinitiator.

Dark polymerization occurs after irradiation is stopped. The change in conversion during the dark polymerization period is expressed as shown in Eq. (4) [20]:

$$-\ln\frac{[M]}{[M]_0} = \frac{k^2}{k_t} \ln(k_t[M^*]_0 t + 1)$$  \hspace{1cm} (4)

where $[M]$ is the molar concentration of the C=C bond at $t$ seconds after irradiation stopped, and is the molar concentration of the macro radical when irradiation stopped.

The pseudo-steady state approximation was applied, and the polymerization rates before and after the stoppage of UV light are equated to determine the values of $k_p$ and $k_t$, respectively, as shown in Eq. (5).

$$-\frac{k_p}{\sqrt{k_t}}[M]_0(1-x)\left(\phi I_0 c[PI]\right)^{0.5} = -[M]_0\frac{k^2}{k_t}k_t[M^*]_0$$  \hspace{1cm} (5)

3. Results

The C=C bond conversion was monitored using real-time FT-IR under three different atmospheres, i.e., purge-to-open, purge, and open atmosphere. Figure 4(a) shows the C=C bond conversion of DPHA after 0.3 s of UV irradiation. As expected, the conversion at 50 s in the open operation is 40% lower than those in the purge-to-open and purge operations. In the open operation, the sample was exposed to air during UV irradiation. Most of the initiator radicals reacted with oxygen, while the remaining initiator radicals reacted with the C=C bond of DPHA. In the purge-to-open and purge operations, almost all initiator radicals reacted with the C=C bond during UV irradiation, as the atmosphere was oxygen-free. The percentage of the initiator radicals that reacted with the C=C bond was smaller in the open operation than in the purge-to-open operation. Therefore, the open operation results in a lower conversion, confirming that the photoinitiator and monomer used in this study were affected by oxygen inhibition, which typically occurs during UV curing.

To compare the results of dark polymerization in the purge-to-open and purge operations, the time-averaged conversion was obtained from the data points in Fig. 4(a) in the range of 50.3±0.325 s. The differences between the two operations are subtle; however, the time-average conversion for the purge-to-open operation (0.358) is lower than that for the purge operation (0.364) at 50 s after stoppage of UV light irradiation. The DDPP value was -0.027, indicating that polymerization was not promoted. In the purge-to-open operation, the sample was exposed to air after irradiation was stopped. The oxygen in air attacked the dangling radical that was formed during the UV irradiation and reduced the C=C bond conversion.

Figure 4(b) shows the results after 1.0 s of UV irradiation. As expected, the conversion for the open operation is much lower than those for the purge-to-open and purge operations. The conversion of the open operation was 0.148 and 0.280 and for irradiation durations of 0.3 and 1 s, respectively. Prolonged UV irradiation enables the supply of more photons and increases the number of initiator radicals created.

Fig. 4. Changes in the C=C bond conversion for DPHA/OXE01 with time under purge, purge-to-open, and open conditions. The UV intensity was 10 mW/cm². The UV irradiation durations are (a) 0.3 s and (b) 1 s.
The results of the purge-to-open and purge operations are interesting. The difference in the time-average conversion between the purge-to-open and the purge operations increases with time: 0.005 at 0 s, 0.006 at 1 s, and 0.013 at 51.0 ± 0.0325 s (purge to open: 0.455, purge: 0.442) after stoppage of irradiation. Therefore, the conversion of the purge-to-open operation increased more prominently than that of the purge after irradiation was stopped. The DDPP was +0.043, indicating that dark polymerization was promoted by exposing the specimen to the oxygen in air. Even though oxygen attacks the dangling radicals and stops the propagation reaction, the relationship between the conversion under purge-to-open and purge in dark polymerization was inverted in magnitude by increasing the duration of UV irradiation from 0.3 to 1 s. The results for different irradiation doses, i.e., 3 and 10 mJ/cm² (Figs. 4(a) and (b)), revealed that the irradiation dose also affects dark polymerization.

Figure 5 shows the conversion of three different monomers and the polymer 50 s after irradiation stopped under the purge-to-open and purge operations. The conversion for the purge-to-open operation became 0.01–0.04 larger than that for the purge when the irradiation dose was above 3 mJ/cm² for DUDM, above 10 mJ/cm² for DPHA, and above 10 mJ/cm² for RP. The conversion for MONO did not show a remarkable difference between these two operations at the same irradiation dose.

To clearly show the difference in conversions between purge-to-open and purge operations under the same irradiation dose, the DDPP defined in Eq. (2) is plotted in Fig. 6. for DPHA, RP, and DUDM.

The magnitude of DDPP for RP is about 10 times greater than those for the other two, which have the same order of magnitude. The negative values of DDPP indicated that the conversion for the purge operation was larger than that for the purge-to-open operation. The purge-to-open operation did not promote polymerization, as indicated by the negative DDPP. These results show that the DDPP increases and then decreases with the irradiation dose, with the peak positions at 5 mJ/cm² for RP, between 3 and 10 mJ/cm² for DUDM, and between 10 and 50 mJ/cm² for DPHA. So, dark polymerization was promoted at a higher irradiation dose up to a threshold value that depended on the monomer.
with increasing irradiation dose when it is greater than 6 mJ/cm². This indicates that the polymerization switched to the diffusion-controlled region from 6 mJ/cm² onward. **RP** does not show this change for irradiation doses over 10 mJ/cm². **DUDM** did not show a clear point at which the switch to the diffusion-controlled region occurred, instead the network structure gradually evolved for irradiation doses over 1 mJ/cm². Therefore, **DPHA**, **RP**, and **DUDM** were all influenced by hindrance by the network structure, and their polymerization was in the diffusion-controlled region for irradiation doses greater than 10 mJ/cm².

Limited hindrance by the network structure.

To clarify the effect of the photoinitiator on the conversion of C=C bonds after switching off the UV light, HCK was used instead of OXE01. Figure 8 shows changes in the C=C bond conversion of the DUDM/HCK mixture. The UV intensity and irradiation time were 10 mW/cm² and 1 s, respectively. It is clearly seen that the conversion of purge is larger than that of purge-to-open. Figure 9 shows the effect of irradiation dose on the conversion of the C=C bond after 50 s. The plots of purge are higher than those of purge-to-open irrespective of the irradiation dose. The promotion of dark polymerization in the purge-to-open operation was not observed for the HCK photoinitiator.

A negative DDPP was observed at the irradiation doses of 3 mW/cm² for **DPHA** and **RP** and 1 mJ/cm² for **DUDM**, as shown in Fig. 6. The irradiation doses for **RP** and **DPHA** correspond to plateaued kinetic constants, where the polymerization was in the reaction rate-controlled region and the network structure was not fully developed. Although the kinetic constant of **DUDM** does not show a plateau, its value at 1 mJ/cm² is at least one order greater in magnitude than those of **RP** and **DPHA**. Therefore, at 1 mJ/cm², the polymerization occurred with only limited hindrance by the network structure.

**Fig. 7.** Kinetic constants for the propagation and termination reactions of **DPHA**, **RP**, and **DUDM**. Photoinitiator was **OXE01**.

**Fig. 8.** Changes in the C=C bond conversion for **DUDM/HCK** with time under purge and purge-to-open. The UV intensity was 10 mW/cm². The UV irradiation durations was 1 s. Data plot was smoothed by the Savitzky-Golay method in the Origin Pro with the window size of 100.

**Fig. 9.** Conversion of C=C bond 50 s after stoppage of UV irradiation under purge (open symbols) and purge-to-open (filled symbols) for the **DUDM/HCK** mixture. The plots of **DUDM/OXE01** were reproduced from Fig. 5 in this paper.
4. Discussion

The impact of oxygen quenching on the network structure is discussed by comparing the results for low and high irradiation doses. Dark polymerization was not enhanced when the irradiation dose was low (i.e., less than 10 mJ/cm²) and the network structure was underdeveloped. Rather, it was enhanced by the purge-to-open operation at a higher UV irradiation dose. The DDPP increased and then decreased with the increase in irradiation dose, indicating that there is an optimal dose to achieve maximum DDPP. At a higher dose, the network structure becomes too dense to enhance polymerization.

Figure 10 schematically illustrates the enhancement of polymerization. At lower irradiation doses, the oxygen from air quenched most of the dangling radicals, which is a typical occurrence in air (open) atmosphere. Dark polymerization was not enhanced by the purge-to-open operation. With the progress of polymerization under UV irradiation, the number of radicals increased and the network structure became dense. When the sample was exposed to air in the purge-to-open operation, the oxygen from air started to quench the dangling radicals. However, the diffusion of oxygen was also slowed down by the dense network structure, and oxygen attack on the radicals was thus suppressed. The surviving radicals underwent polymerization, while the oxygen-quenched (dead) radicals did not contribute to the formation of the cross-linking network. The hindrance to other radicals by the dangling chain of the quenched radicals was weaker than the hindrance by the network structure. Meanwhile, the quenching radicals generated sufficient free volume to allow polymerization of the surviving radicals. However, with increasing irradiation dose, this effect became less pronounced since the dense network did not possess enough free volume to polymerize the surviving radicals.

The maximum DDPP of RP was one order of magnitude higher than those of the other monomers. This could be explained by the molar concentration of the polymerizable functional groups. As shown in Table 1, this concentration for the reactive polymer is 3.76, the lowest among the monomers. As a result, the network structure is not dense. Indeed, in Fig. 7, the corresponding kinetic constants for irradiation doses above 30 mJ/cm² are higher than those for the other monomers. As shown in Fig. 11, the polymerization of the dangling radicals is easier since it is less hindered by the network structure.

MONO did not show enhancement in polymerization, because it did not form a chemical cross-linking structure, and so there was only limited decrease in the diffusion rate of oxygen. Most radicals were quenched immediately after the purge-to-open operation.

In summary, dark polymerization is likely to be enhanced in a purge-to-open operation with multifunctional monomers having a low molar concentration of the functional group.

The comparison of the photoinitiators OXE01 and HCK showed that dark polymerization was only exhibited by OXE01 owing to the higher reactivity and lower oxygen inhibition of OXE01 compared to those of HCK [22].

5. Conclusion

This study investigated the impact of oxygen quenching of dangling radicals on the conversion of C=C bonds, by changing the UV irradiation dose and atmosphere after UV irradiation. When polymerization occurred in the diffusion-controlled region, the polymerization of DPHA, RP, and DUDM was enhanced to 0.01–0.04 upon exposure to air. It was supposed that the oxygen quenching of some of the dangling radicals stopped the
polymerization, but generated sufficient free volume for the surviving dangling radicals to polymerize. An optimal irradiation dosage was identified to realize the maximum conversion of the C=C bond, where the density of network structure and number of macro radicals. This study uses real-time FT-IR measurements to discusses the effect of the network structure on C=C bond conversion by considering the kinetic constants. Although direct experimental observation of the network structure is still limited, stochastic modeling would be a powerful tool to investigate network structures that are partially quenched with oxygen and to develop ways to promote polymerization. The results observed for dark polymerization showed dependence on the type of photoinitiator. When a highly reactive photoinitiator with low oxygen inhibition is used, the role of the network structure in the purge-to-open operation is prominent.

Acknowledgements
This work was partly supported by a Grant-in-Aid for projects to support the advancement of strategic core technologies in contingency reserve of fiscal 2010, from MITI, Japan, JSPS KAKENHI for Scientific Research on Innovative Areas “MFS Materials Science (grant number JP18H05483). JSPS KAKENHI grants (numbers 16K14469 and 18K04823). We would like to thank Editage (www.editage.com) for English language editing.

References
1. R. Schwalm, “UV Coatings: Basic, Recent Developments and New Application”, 1st edition ed.; Elsevier: Amsterdam (2007).
2. S. C. Ligon, B. Husár, H. Wutzel, R. Holman, and R. Liska, Chem. Rev., 114 (2013) 557.
3. G. Odian, “Principles of Polymerization”, Wiley & Sons: New York (1991).
4. J. F. Rabek, “Experimental and Analytical Methods for the investigation of Radiation Curing”, “Radiation Curing in Polymer Science and Technology”, Elsevier: London (1993) Vol. 1, p329.
5. K. S. Anseth and C. N. Bowman, Chem. Eng. Sci., 49 (1994) 2207.
6. K. S. Anseth and C. N. Bowman, J. Polym. Sci. B: Polym. Phys., 33 (1995) 1769.
7. K. A. Berchtold, T. M. Lovestead, and C. N. Bowman, Macromolecules, 35 (2002) 7968.
8. J. A. Burdick, T. M. Lovestead, and K. S. Anseth, Biomacromolecules, 4 (2003) 149.
9. T. M. Lovestead, A. K. O’Brien, and C. N. Bowman, J. Photochem. Photobiol., A, 159 (2003) 135.
10. T. M. Lovestead, K. A. Berchtold, and C. N. Bowman, Macromolecules, 38 (2005) 6374.
11. T. M. Lovestead and C. N. Bowman, Macromolecules, 38 (2005) 4913.
12. T. M. Lovestead, J. A. Burdick, K. S. Anseth, and C. N. Bowman, Polymer, 46 (2005) 6226.
13. K. Taki, T. Taguchi, R. Hayashi, and H. Ito, J. Photopolym. Sci. Technol., 30 (2017), 413.
14. M. Wen, L. E. Scriven, and A. V. McCormick, Macromolecules, 36 (2003) 4151.
15. M. Wen, L. E. Scriven, and A. V. McCormick, Macromolecules, 36 (2003) 4140.
16. K. Taki, Y. Watanabe, H. Ito, and M. Ohshima, Macromolecules, 47 (2014) 1906.
17. K. S. Anseth and C. N. Bowman, Polym. React. Eng., 1 (1992-93) 499.
18. D. L. Kurdikar, and N. A. Peppas, Macromolecules, 27 (1994) 4084.
19. M. D. Goodner, H. R. Lee, and C. N. Bowman, Ind. Eng. Chem. Res., 36 (1997) 1247.
20. E. Andrzejewska, Prog. Polym. Sci., 26 (2001) 605.
21. A. Tsuneishi, S. Uchiyama, R. Hayashi, K. Taki, and T. Kozawa, Jpn. J. Appl. Phys., 57 (2018) 096501
22. K. Dietliker, T. Jung, J. Benkhoff, H. Kura, G. Geisheidt, and G. Rist, Macromol. Symp., 217 (2004) 77.