

Near Ultraviolet-Sensitive Polyurethanes Networked with Photolabile Carbamoyloxime Linker Units

Kanji Suyama^{1*} and Hideki Tachi²

¹ Faculty of Liberal Arts and Sciences, Osaka Prefecture University,
1-1 Gakuencho, Nakaku, Sakai, Osaka 599-8531, Japan,

² Research Division of Polymer Functional Materials,
Osaka Research Institute of Industrial Science and Technology,
7-1 Ayumino-2, Izumi, Osaka 594-1157, Japan,

*suyama@las.osakafu-u.ac.jp

Photolabile crosslinking units can provide drastic changes of many properties of networked polymers. Herein polyurethanes (PUs) networked with photolabile *O*-carbamoyloxime units were prepared and characterized. The PUs were made of hexamethylene diisocyanate (HDI), polyethylene glycol (PEG), and truxenone trioxime whose absorption band reached 450 nm. The molar ratio of [NCO] in HDI / [OH] in PEG / [OH] in oxime was 1.10 / 0.967 / 0.033 in feed. Obtained PU was an elastic film with 3 mm thickness and 96 % of gel fraction. On irradiation with Hg-Xe lamp, the gel fraction slightly decreased. Also, the decrease in viscoelastic parameters was observed when irradiated at 365 nm in a photorheometer, showing slight degradation of networked structure on near UV-irradiation. The ATR spectra of irradiated surface showed the disappearance of a small peak around 1760 cm⁻¹, suggesting the photodegradation of *O*-carbamoyloxime units proceeded.

Keywords: Near UV sensitive, Carbamoyloxime, Decrosslink, Photolabile crosslinker, Polyurethane, Rheometer

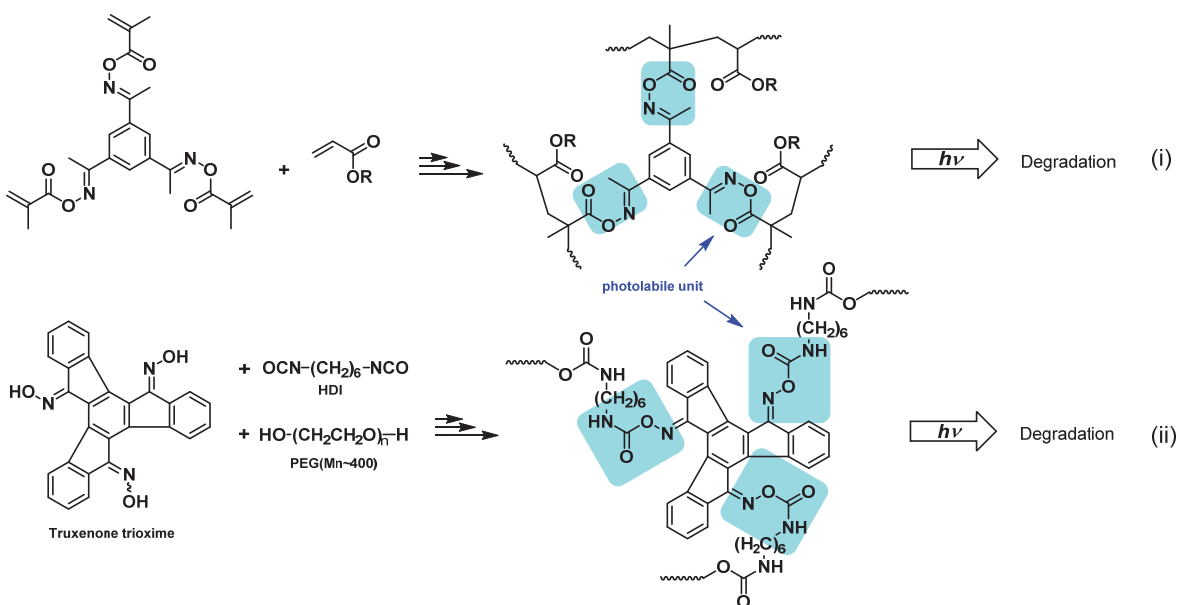
1. Introduction

Decrosslinking is an event that causes drastic changes in many excellent properties of networked polymers. Stimuli-induced decrosslinking techniques are thus useful for the design of functional materials [1,2]. When light is used as the stimulus, easy spatiotemporal control, small damage on substrates, and remote activation are possible [3].

We have been studying photolabile crosslinkers based on *O*-acyloxime units that enable easy introduction in the networked polymers by free-radical polymerization [4]. By using these crosslinkers, we succeeded in the formation and degradation of the networked structure as shown in Scheme 1(i) [5], which was then applied to photo-induced debonding of pressure-sensitive adhesives [6]. Also, we have tried to sensitize this system to near UV region that is advantageous in the use for bio-related, pigmented, and aromatics-containing systems. The photoreactions of *O*-acyloxime units

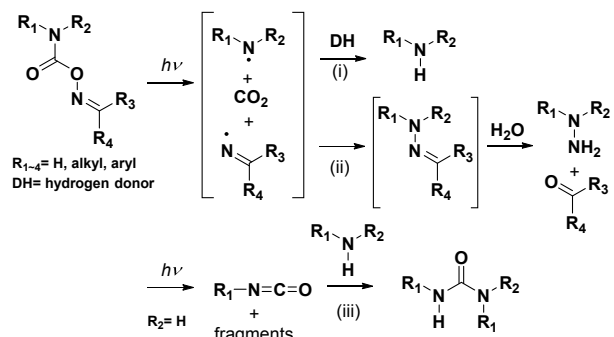
proceeded in the presence of a sensitizer with >310 nm of light, which was confirmed by means of direct observation in viscoelastic parameter changes using a photorheometer [7,8].

In this communication, we report the results of preparation and evaluation of polyurethanes (PUs) whose crosslinking points are linked with photolabile units. PUs are widely used in many applications such as elastomers, flexible and rigid forms, coatings, and adhesives [9]. Photo-induced degradation of PUs has been reported, where diols containing photolabile *o*-nitrobenzyl [10-13] moieties were mainly incorporated as photolabile units. PUs are often prepared from addition reactions of polyols and isocyanates. Therefore, we incorporate urethane linkages composed of oximes and isocyanates. Resulting *O*-carbamoyloxime units are known as photolabile units as well as *O*-acyloximes [14]. So far, the photodegradation of polymers containing *O*-carbamoyloxime [15] and *O*-carbamoylphthalimido



Scheme 1. Proposed formation and photodegradation reactions of polymers in (i) previous and (ii) this work.

[16] units in main-chains was reported. Chae [17], Allonas [18] and their coworkers clarified the aminyl radical formation followed by hydrogen abstraction as shown in Scheme 2 (path i) based on laser flash photolysis studies. Product analyses supported this mechanism and other reactions such as paths (ii) and (iii) [19-21].



Scheme 2. Proposed photoreactions of *O*-carbamoyloximes in literatures.

As a starting oxime, we selected truxenone trioxime as shown in Scheme 1(ii). Truxenone and its derivatives have been studied as precursors of fullerene fragments [22] and as chromophores of photoinitiators that absorb near UV region of light or two photon photochemistry [23,24]. In the present study, we also used truxene skeleton as a chromophore for near UV region.

2. Experimental

2.1. Instruments

NMR, UV-vis, IR, and fluorescence spectra were recorded by a Jeol JNM-ECX400, Shimadzu UV2400PC, Jasco FTIR4200, and Jasco FR6500

spectrometers, respectively. Mass spectrum was measured by a Thermo Fischer Scientific Q-Extractive. Melting point was obtained by using a Yanako MT-S3 melting point apparatus. Rheological experiments were performed with a Thermo Scientific HAAKE MARS III rotational rheometer. Light intensity was measured by an Orc UV-M03 illuminometer.

2.2. Materials

Truxenone was obtained by heating indane-1,3-dione in conc. H₂SO₄ as described in literature [25]. Aliquot was recrystallized from chloroform for UV-vis spectra measurement. Pyridine, hexamethylene diisocyanate (HDI), 1,8-diazabicyclo[7.4.0]dec-7-ene (DBU), and polyethylene glycol (PEG, average Mn ≈ 400) were used as received from Nacalai Tesque (Kyoto, Japan).

2.3. Truxenone trioxime

In a flask, 15.0 g (39.02 mmol) of truxenone, 12.2 g (176 mmol) of hydroxylamine hydrochloride, and 300 mL of pyridine were heated at 100 °C for 24 h. After rotavaping, the mixture was added 200 mL of ionized water and filtered to afford 18.6 g of dark amber powder. Yield: 91.5 %. Melting point: > 300 °C. ¹H NMR (DMSO-d₆): δ 7.41 (6H, s, aromatic), 8.58 (3H, d, aromatic), 9.45 (3H, s, aromatic), 12.87 (3H, s, OH). ¹³C NMR (DMSO-d₆): δ 122.081, 123.062, 123.885, 124.711, 125.073, 125.131, 130.190, 131.780, 142.776. IR (KBr): 3489, 3464 (asymmetric), 3000 ~ 3500 1633, 1599, 1561, 1454, 1427, 1387, 967 cm⁻¹. High

Resolution MS(ESI) m/z : $[M+H]^+$ calcd for $C_{27}H_{16}N_3O_2$ 430.1192; found 430.1202. UV (CH₃OH): λ_{max} 249.6 (molar absorption coefficient ϵ : 7.83×10^4), 291.0 (3.51×10^4), 337.3 (2.10×10^4), and 365.0 nm (1.56×10^4 L·mol⁻¹·cm⁻¹).

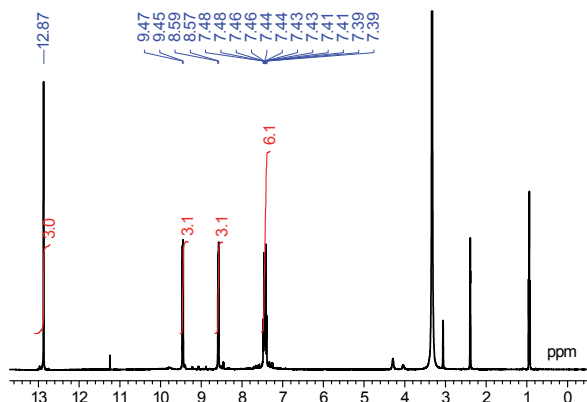


Fig. 1. ¹H NMR (DMSO-*d*₆) spectrum of truxenone trioxime.

2.4. Preparation of PUs

In a flask, 13.50 g (33.8 mmol) of PEG was dissolved in 10 mL of toluene and heated on a hot plate to remove moisture azeotropically. To the residue, 10 mL of toluene and 2 mL of pyridine was added again and heated until most of solvents were removed. Then, the mixture was cooled to ambient temperature with stirring under N₂ flow, added 334 mg (0.778 mmol) of truxenone trioxime, and 46 μ L of DBU using a dispenser. Then, 6.20 mL of HDI (38.34 mmol) was added in one portion, stirred for a few minutes, and cast on a dish made of tetrafluoroethylene-perfluoroalkylvinyl ether copolymer (70 mm x 100 mm). The mixture was soon degassed in a desiccator and stored for 8 days at room temperature. Then the film was removed from the dish and heated at 100 °C on PTFE sheet for 1 h.

2.5. Evaluation of PUs

For the measurement of gel fractions, films were cut into short strips (1~3 mm x ca. 3 mm x 20~30 mm, total ca. 250 mg) and irradiated with a Hayashi LA410 mercury xenon lamp. In order to irradiate all sides, the strips were turned occasionally during the irradiation. Then the strips were extracted with chloroform for 2 h using a small Soxhlet kit.

For rheological measurements, sample films (discs) were placed between parallel plates and applied an oscillation with a constant frequency at 1 Hz under a constant strain amplitude ($\gamma = 0.01$) in the rheometer. During the measurement, films were in-situ heated or illuminated at 25 °C with 365

nm LED light which was introduced through a quartz bottom plate. Attenuated total reflection-IR (ATR-FTIR) spectra of the film before and after irradiation were measured using a Jasco ATR Pro450-S attachment (single reflection, angle of incidence: 45°) with a prism of Ge crystal.

3. Results and discussion

3.1. Synthesis and characterization of truxenone trioxime

Truxenone trioxime could be prepared by heating with excess hydroxylamine in pyridine. Obtained solid showed a ¹H NMR spectral peak at 12.87 ppm due to OH groups in Fig. 1, and had no IR peak at 1713 cm⁻¹ which was found in truxenone due to C=O stretching band as shown in Fig. 2. Although two isomers (*E,E,E*) and (*E,E,Z*) for three C=N bonds are possible, it is unclear whether these isomers are mixed or not.

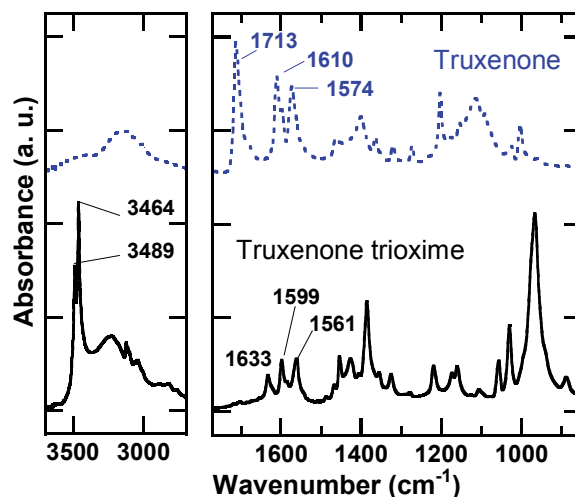


Fig. 2. IR (KBr) spectra of truxenone (upper) and truxenone trioxime (lower).

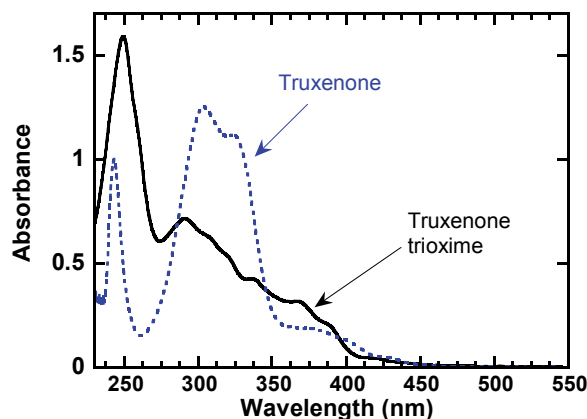


Fig. 3. UV spectra of 2.0×10^{-5} M solutions of truxenone (chloroform) and truxenone trioxime (methanol).

Figure 3 shows UV-visible spectra of truxenone and truxenone trioxime. The former showed strong peaks at 304 and 324 nm due to aromatic ketone as literature [26]. Trioxime has not such a strong peak above 300 nm, although absorption band reached 450 nm, and ϵ at 405 and 436 nm were 3.15×10^3 and $1.08 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, respectively.

Truxenone trioxime emitted fluorescence as shown in Fig. 4. This result suggests that *O*-carbamoyloxime units in PUs also emit fluorescence.

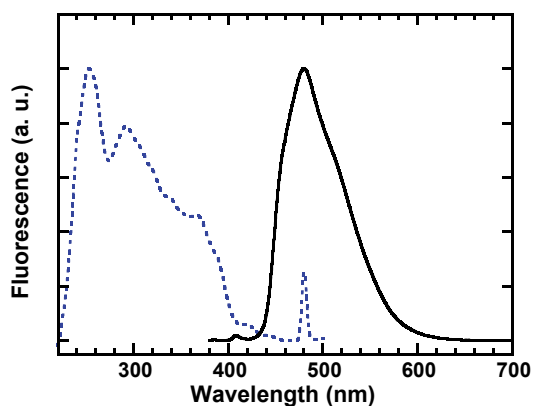


Fig. 4. Fluorescence emission (excited at 365 nm) and excitation (excited at 480 nm) spectra of 2.0×10^{-5} M methanol solution of truxenone trioxime.

3.2. Synthesis and characterization of PU film

PUs were prepared by addition reaction of HDI with PEG and truxenone trioxime in a molar ratio of $[\text{NCO}]$ in HDI / $[\text{OH}]$ in PEG / $[\text{OH}]$ in oxime = 1.10 / 0.967 / 0.033. DBU was used as a catalyst instead of conventional organotin compounds according to the literature [27] and worked well for the formation of PUs. Obtained resin was a brownish elastic sheet with ca. 3 mm thickness. The ATR-FTIR spectrum of the PU is shown in Fig. 5, where characteristic peaks due to urethane C=O stretching and N-H bending bands are found around 1730 and 1500 cm^{-1} , respectively. In addition, a small shoulder at 1760 cm^{-1} is also confirmed.

Thermal property of PU discs was investigated by using a rheometer with in-situ heating. Figure 6 shows the profiles of storage (G') and loss (G'') moduli, absolute value of complex viscosity ($|\eta^*|$), and $\tan \delta (= G''/G')$ on heating. The simultaneous decrease in G' , G'' , and $|\eta^*|$ along with an increase in $\tan \delta$ is found at 50 $^{\circ}\text{C}$, which is a behavior often observed at glass transition temperature. Above 130 $^{\circ}\text{C}$, similar but remarkable changes are observed, suggesting thermal degradation proceeded. The latter is consistent with thermal dissociation character of *O*-carbamoyloximes into

isocyanates and oxime as reported previously [21].

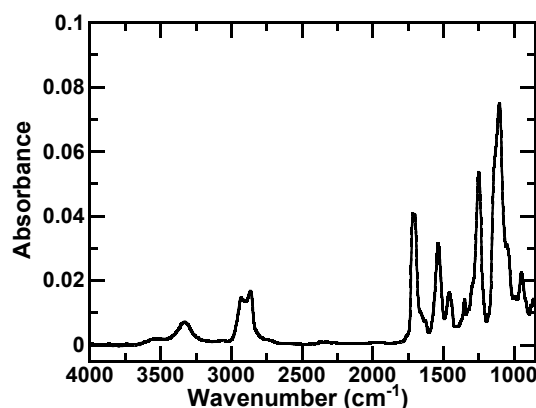


Fig. 5. ATR-FTIR spectrum of PU.

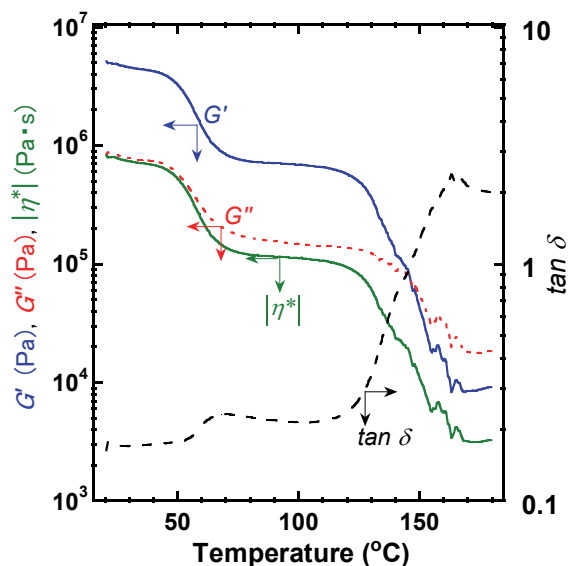


Fig. 6. Changes of viscoelastic parameters of non-irradiated PU on heating at 5 $^{\circ}\text{C}/\text{min}$. Sample disc: 3mm thickness.

In order to confirm the networked structure, gel fraction of the PU was measured by extracting with chloroform. Non-irradiated PU showed the gel fraction of 96%, showing the formation of networked structure.

Table 1. Gel fractions of PU on irradiation^a

Irradiation time (min)	Gel fraction ^b (%)
0	96
5	93
10	92
25	86
60	89

a) Hg-Xe lamp, light intensity 250 mW/cm^2 at 365 nm.
b) Weight ratio before and after Soxhlet extraction for 2 h in chloroform.

PU samples irradiated with Hg-Xe lamp were also applied to Soxhlet extraction, and found that gel fractions tended to decrease on irradiation as shown in Table 1. This result suggests that the slight degradation of PU proceeded on irradiation.

We further investigated viscoelastic parameters changes during irradiation at 365 nm. As shown in Fig. 7, G' , G'' , and $|\eta^*|$ gradually decreased on irradiation and finally reduced by 31, 22, and 29 % from their maximum values, respectively. This result was consistent with that obtained from gel fraction measurement, suggesting the slight degradation of networked structure. During the measurement, fluorescence from irradiated side of the PU disc was observed, and its color gradually changed as an increase in irradiation time.

Figure 8 shows ATR-FTIR spectra of the PU disc. A shoulder at 1760 cm^{-1} found in non-irradiated PU disappeared after irradiation. These results strongly suggest that the change of chemical structure indicating a peak at 1760 cm^{-1} contribute to the degradation of networked structure. This shoulder peak might be assignable to C=O stretching band in *O*-carbamoyloximes, because they appeared at $1735\sim 1760\text{ cm}^{-1}$, depending on its structure [21].

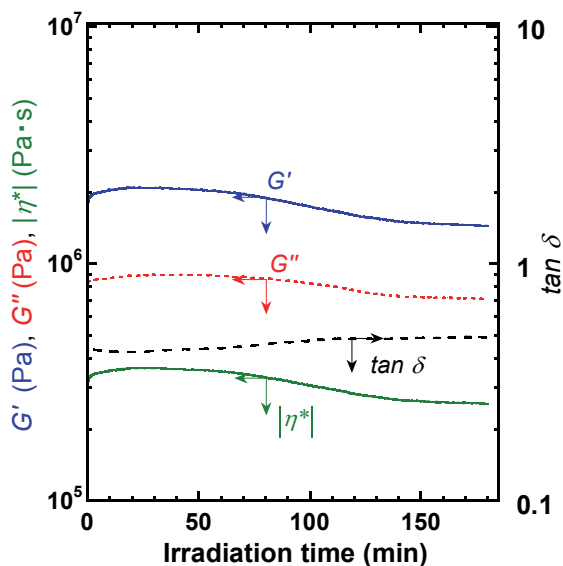


Fig. 7. Changes of viscoelastic parameters of PU on irradiation with 365 nm LED light whose intensity was 41 mW/cm^2 .

In this study, irradiated light was absorbed only near the surface due to strong absorption of trioxime units. However, considering the light intensities used in solubility and rheological studies, the photoreaction seems slow. One possible reason is the emission from truxene core which consumes

excited energy and reduces the photoreaction of *O*-carbamoyloxime units. Although we have not estimated, the quantum yield of fluorescence might be high. The recombination of *O*-carbamoyloxime units after photolysis and the existence of physical crosslinking point might contribute to the slow changes of bulk properties.

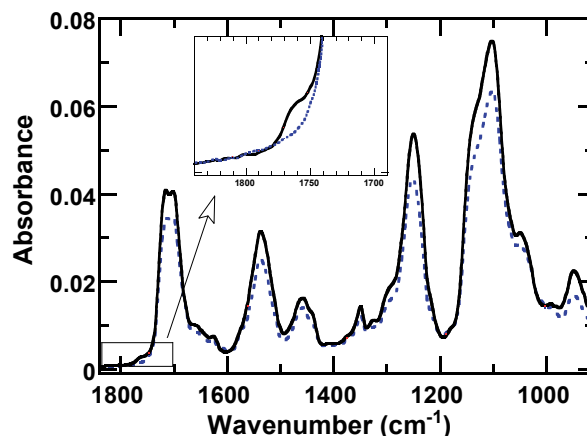


Fig. 8. ATR-FTIR spectra of PU discs. Before (—), and (.....) after (irradiated side) irradiation.

4. Conclusion

We could prepare networked PU film containing truxeneon trioxime with *O*-carbamoyloxime moieties as shown in Fig. 1. Resulting PU was sensitive to near UV-light, although its solubility and viscoelastic property changes were slow than expected. However, fluorescent and hydrophilic nature might be useful in some applications.

In forthcoming paper, we are planning to clarify the spectral changes of model compound of truxeneon-based *O*-carbamoyloxime on irradiation.

Acknowledgement

We thank to Dr. Hirokazu Hayashi of Chemical Environment Section, Technology Research Institute of Osaka Prefecture for his support in MS measurement, and JSPS for financial aid (KAKENHI Grant Number 25340095).

References

1. M. Shirai, *Prog. Org. Coat.*, **58** (2007) 158.
2. C. J. Kloxin and C. N. Bowman, *Chem. Soc. Rev.*, **42** (2013) 7161.
3. O. Bertrand and J. -F. Gohy, *Polym. Chem.*, **8** (2017) 52.
4. K. Suyama and H. Tachi, *J. Photopolym. Sci. Technol.*, **27** (2014) 231.
5. K. Suyama and H. Tachi, *RSC Adv.*, **5** (2015) 31506.

6. K. Suyama and H. Tachi, *J. Photopolym. Sci. Technol.*, **28** (2015) 45.
7. K. Suyama and H. Tachi, *J. Photopolym. Sci. Technol.*, **29** (2016) 139.
8. K. Suyama and H. Tachi, *Prog. Org. Coat.*, **100** (2016) 94.
9. H. -W. Engels, H. -G. Pirkel, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann, and J. Dormish, *Angew. Chem. Int. Ed.*, **52** (2013) 9422.
10. D. Han, X. Tong, and Y. Zhao, *Macromolecules*, **44** (2011) 437.
11. C. Lv, Z. Wang, P. Wang, and X. Tang, *Langmuir*, **28** (2012) 9387.
12. L. García-Fernández, A. Specht, and A. del Campo, *Macromol. Rapid Commun.*, **35** (2014) 1801.
13. L. García-Fernández, C. Herbivo, V. S. M. Arranz, D. Warther, L. Donato, A. Specht, and A. del Campo, *Adv. Mater.*, **26** (2014) 5012.
14. K. H. Chae, *Macromol. Rapid Commun.*, **19** (1998) 1.
15. E. C. Buruiana, M. Olaru, and B. C. Simionescu, *J. Appl. Polym. Sci.*, **94** (2004) 2324.
16. M. Tian, R. Cheng, J. Zhang, Z. Liu, Z. Liu, and J. Jiang, *Langmuir*, **32** (2016) 12.
17. H. Hwang, D. J. Jang, and K. H. Chae, *J. Photochem. Photobiol. A: Chem.*, **126** (1999) 37.
18. J. Lalevee, X. Allonas, J. -P. Fouassier, H. Tachi, A. Izumitani, M. Shirai, and M. Tsunooka, *J. Photochem. Photobiol. A: Chem.*, **151** (2002) 27.
19. K. H. Chae, H. I. Cho, Y. H. Kim, and U. C. Yang, *Eur. Polym. J.*, **48** (2012) 1186.
20. M. Tsunooka, H. Tachi, K. Asakino, and K. Suyama, *J. Photoscience*, **6** (1999) 145.
21. K. Suyama, S. Nakao, and M. Shirai, *J. Photopolym. Sci. Technol.*, **18** (2005) 141.
22. F. Goubard and F. Dumur, *RSC Adv.*, **5** (2015) 3521.
23. M. T. Nguyen, J. -P. Tremblay-Morin, and P. Gaudreault, WO 2012/159213 A1.
24. M. -A. Tehfe, F. Dumur, E. Contal, B. Graff, D. Gigmes, J.-P. Fouassier, and J. Lalevée, *Macromol. Chem. Phys.*, **214** (2013) 2189.
25. E. V. Dehmlow and T. Kelle, *Syn. Commun.*, **27** (1997) 2021.
26. M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.*, **20** (1972) 343.
27. H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail, and J. L. Hedrick, *Macromolecules*, **48** (2015) 3153.