

# Refractive index evolution of various commercial acrylic resins during photopolymerization

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**Abstract.** A set of commercial (meth)acrylic resins was photopolymerized under identical irradiation conditions and evolution of their refractive index was monitored as a function of double bond conversion. Initial refractive index values ranged from 1.4445 to 1.5454 and then linearly increased with conversion as long as the material was not in the glassy state. This increase was related to an increase of the material density arising during polymerization. Final refractive index values ranged from 1.4804 to 1.5632. The knowledge of the refractive index and of its evolution during the photocuring is indispensable, in particular to elaborate composite materials (polymer matrix + filler) with well controlled optical properties.

**Keywords:** industrial applications, photopolymerization, acrylic resin, refractive index

## 1. Introduction

Nowadays, acrylic materials are widely present in various application fields and many commercial resins are available on the market. If these acrylic resins are currently used to elaborate photocured materials, they can also be mixed with (in)organic fillers to obtain composite materials for dental applications [1–4], paints [5, 6], ceramics [7–10]. The main shortcoming of the photopolymerization process applied to composite formulations is the low depth of cure due to the limited light penetration resulting from scattering by fillers and filler-matrix interface. Theoretical and experimental results have shown that matching filler and organic matrix refractive indices leads to a decrease in the light scattering phenomenon [11–14]. Because of the acrylic matrix volume shrinkage consecutive to its photopolymerization, it is noteworthy that the refractive index of this matrix increases, whereas the refractive index of filler is supposed to be constant. If the refractive index of (meth)acrylic resins is often known, its evolution

during their polymerization is never specified in the technical datasheets. However, these data are essential for applications in need of well controlled optical properties (holographic data-storage (HDS) technologies [15], transparent glass cloth reinforced plastics [16], gradient-index (GRIN) optics [17], transparent fiber glass reinforced composites [18] etc), as well as for the elaboration of thick homogeneous composite materials, where the prediction of the cure light transmission evolution and its influence on conversion profiles and cure depth is fundamental [19].

This work aims to characterize the refractive index evolution of some usual and commercial photocurable (meth)acrylic resins. For that, refractive index, double bond conversion, mechanical transition temperature  $T_{\alpha}$  and material density were measured versus irradiation time. The paper will be decomposed in two parts. In the first part, an aromatic dimethacrylate resin (Bis-GMA) was chosen to accurately describe the experimental process used. In the second

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part, results obtained on the set of commercial resins were discussed.

## 2. Materials and methods

### 2.1. Materials

Tripropylene glycol diacrylate (TPGDA, Sigma-Aldrich), triethylene glycol dimethacrylate (TEGDMA, Sigma-Aldrich, 95%), polyethylene glycol (200) dimethacrylate (PEG200DMA, Sigma Aldrich), pentaerythritol triacrylate (PETA, Sigma-Aldrich), Bisphenol A glycidyl dimethacrylate (Bis-GMA, Sigma-Aldrich, 99%) were used as received. Photomer 5429, Photomer 3015 and Photomer 3016 were kindly supplied by IGM Resins (Cognis). Crodamer UVP215 and Crodamer (UVP220) were purchased from ex-Croda. Ebecryl 836, Ebecryl 851, Ebecryl 1608, Ebecryl 605 and Ebecryl 3700 were kindly supplied by UCB Chemicals. Dipropylene glycol diacrylate (DPGDA), ethoxylated 3 bisphenol A dimethacrylate (BPA3EODMA), CN104C75 and CN104Y50 were kindly supplied by Sartomer. Laromer 8800, Laromer 8986 and Irgacure 819 were kindly supplied by BASF. All these resins were used as received.

1 wt% Irgacure 819 was added in each resin and the mixture was stirred at room temperature.

### 2.2. Methods

#### 2.2.1. Conversion and refractive index measurements

The polymerization progress was monitored at 30 °C by real time infrared spectroscopy using a Vertex 70 FTIR spectrometer (Bruker). An attenuated total reflection accessory (ATR MKII Golden Gate, Specac, Eurolabo) was used. A drop of the photocurable mixture was spread out over the ATR crystal and covered by a polyethylene film and a quartz plate in order to assure uniform exposed surface and to avoid the reaction inhibition caused by oxygen. The absorbance measured for each functional group was determined by the area ( $A$ ) of the corresponding absorption peak. The conversion  $\chi$  was then calculated using the ratios of the (meth)acrylic double bond absorbance ( $A^{\text{function}}$ ) at 1636 or 809  $\text{cm}^{-1}$  to the reference absorbance ( $A^{\text{ref}}$ ) corresponding to the aromatic cycle at 1607  $\text{cm}^{-1}$  for aromatic resins or to the C–O band at 1452  $\text{cm}^{-1}$  for aliphatic resins according to Equation (1):

$$\chi(t) = \frac{\frac{A_0^{\text{function}}}{A_0^{\text{ref}}} - \frac{A_t^{\text{function}}}{A_t^{\text{ref}}}}{\frac{A_0^{\text{function}}}{A_0^{\text{ref}}}} \quad (1)$$

where  $A_0$  is the initial area and  $A_t$  is the area of the peak at  $t$  time.

The refractive index evolution was followed at 30 °C by real time refractometry at 656 nm using an Arago refractometer (Cordouan Technologies). The formulation was spread out over the Sapphire prism without adding any high refractive index interfacial contact agent.

The light intensity coming from a 365 nm light emitting diode was measured at the sample surface using a radiometer (Vilber - Intraspex Oriel VLX-3W).

#### 2.2.2. Density measurement

Material density was measured at 20 °C with an Archimedean balance (Scaltec analytical balance fitted with a density determination kit appropriate to an accuracy to  $10^{-4}$  g).

#### 2.2.3. Mechanical transition temperature measurement

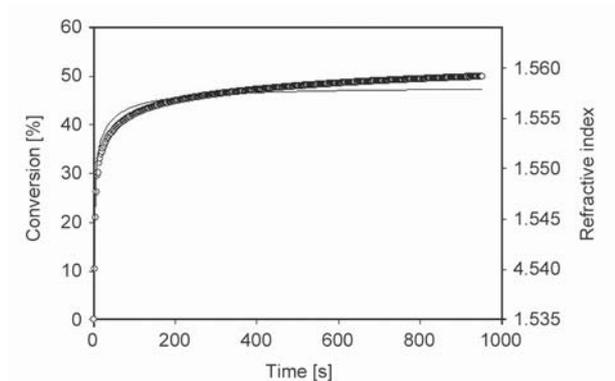
Photocured samples were analyzed by dynamical mechanical analysis (DMA Q800, TA Instruments) in compression mode using a stainless steel parallel plate probe at a 1 Hz frequency and a 3 °C/min heating rate. The applied strain amplitude was 5  $\mu\text{m}$ . The mechanical transition temperature  $T_\alpha$  was measured at the maximum of the  $\tan\delta$  curve.

## 3. Results and discussion

### 3.1. Description of the experimental process

Bis-GMA was first irradiated with a 20  $\text{mW}\cdot\text{cm}^{-2}$  light intensity in the presence of 1 wt% Irgacure 819. The photopolymerization reaction was monitored in real time by infrared spectroscopy and refractometry. Figure 1 shows that the refractive index value evolved versus time in the same way that double bond conversion.

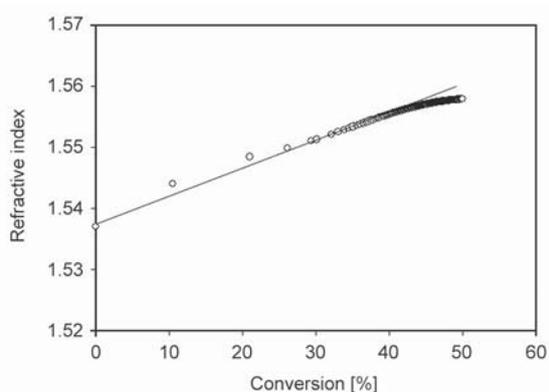
In a general way, the refractive index value of a given material depends on two parameters: the material density and its polarisability [20]. However, it is well known that, in the course of the photopolymerization, the volume shrinkage increases the material density, whereas the polarisability of the molecule decreases (evolution from a double carbon-carbon



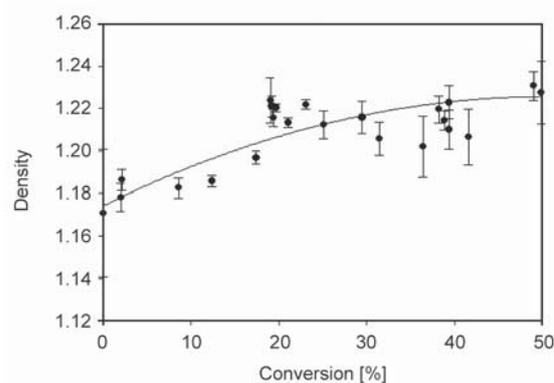
**Figure 1.** (—) refractive index and (o) double bond conversion of Bis-GMA versus irradiation time ( $T = 30^{\circ}\text{C} - I_0 = 20 \text{ mW}\cdot\text{cm}^{-2}$ ).

bond towards single carbon-carbon bond). Hence, the evolution of the two parameters modify the refractive index value of the reaction mixture in an antagonist way. Experimental results revealed an increase in the refractive index value, meaning that the material density prevailed over the polarisability, as already mentioned [11, 14, 21–23]. The evolution of the material density versus double bond conversion was measured to confirm this assumption (Figure 2).

The combination of both refractive index and conversion evolution curves by elimination of the time parameter allowed plotting the relationship between conversion and refractive index in the course of the UV exposure (Figure 3). One can observe that linear relationships was obtained at conversion lower than 40%. Above this value, the reaction continued but the refractive index remained constant. This can be related to the material density evolution (Figure 2). Indeed, the density of Bis-GMA, as its refractive index, became constant when conversion reached 40%. Let us remind that



**Figure 2.** Refractive index-conversion relationship for Bis-GMA ( $T = 30^{\circ}\text{C} - I_0 = 20 \text{ mW}\cdot\text{cm}^{-2}$ ).



**Figure 3.** Density-conversion relationship for Bis-GMA ( $T = 30^{\circ}\text{C} - I_0 = 20 \text{ mW}\cdot\text{cm}^{-2}$ ).

the maximal double bond conversion is limited by the material vitrification [24].

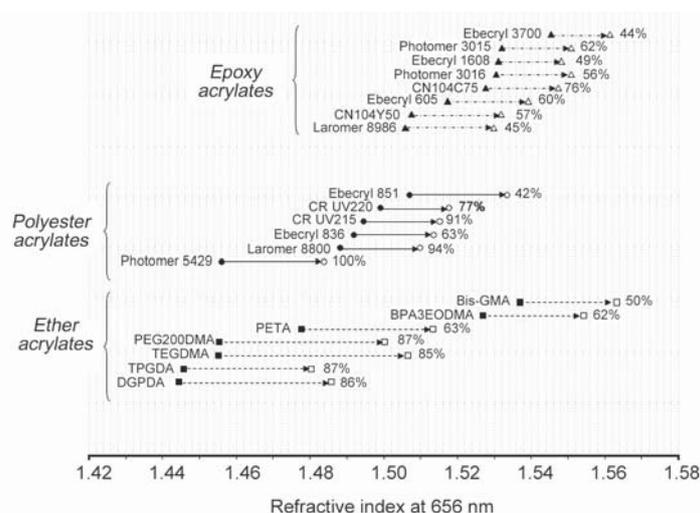
### 3.2. Discussion of the physicochemical characteristics of commercial resins

Several resins belonging to three great families of acrylic resins were selected: ether acrylates, polyester acrylates and epoxy acrylates (Table 1). Each one was photopolymerized in the presence of 1 wt% Irgacure 819 with a  $200 \text{ mW}\cdot\text{cm}^{-2}$  UV light intensity and photocured materials were analyzed by infrared spectroscopy, refractometry and DMA. Final double bond conversion, initial and final refractive indices and mechanical transition temperature  $T_{\alpha}$  of the materials are collected on Figure 4 and Table 1. Firstly, one can observe that, before photopolymerization, the initial refractive index value of (meth)acrylic resins is ranging from 1.4445 and 1.5454. As aforementioned, the intrinsic refractive index of a resin depends on its density and on its chemical structure (nature of atoms and chemical bonds), and more especially, on the polarisability of the molecule [20]. Thus, the contribution of simple covalent bond to the molecule polarisability is lower than the contribution of aromatic rings [25]. This is the reason why the lower values were obtained for aliphatic resins and the higher for aromatic ones. Moreover, the refractive index increase consecutive to the polymerization reaction is greater for ether acrylates ( $\Delta n$  from 0.035 to 0.051 for aliphatic resins with final double bond conversion ranging from 63 to 87% –  $\Delta n$  about 0.027 for aromatic resins with final double bond conversion ranging from 50 to 62%) than for polyester acrylates ( $\Delta n$  from 0.019 to 0.027 with final double bond conversion ranging from 42 to 100%) and epoxy acrylates ( $\Delta n$  from 0.016 to 0.024 with final double bond conversion

**Table 1.** Physicochemical characteristics of commercial (meth)acrylic resins before and after photopolymerization ( $I_0 = 200 \text{ mW} \cdot \text{cm}^{-2}$ ).

Commercial name (purchaser)	Chemical composition	Molar mass <sup>(a)</sup> [g·mol <sup>-1</sup> ]	Density <sup>(a)</sup> at 25 °C	Refractive index <sup>(b)</sup> at 656 nm			Double bond conversion <sup>(c)</sup> [%]	$T_g$ <sup>(d)</sup> [°C]
				Before UV	After UV	$\Delta n$		
<b>Ether acrylates</b>								
DPGDA / SR 508 (Sartomer)	Dipropylene glycol diacrylate	242	1.05	1.4445	1.4858	0.0358	86	45
TPGDA (Sigma-Aldrich)	Tripropylene glycol diacrylate	300	1.03	1.4458	1.4804	0.0346	87	54
TEGDMA (Sigma-Aldrich)	Triethylene glycol dimethacrylate	286	1.09	1.4552	1.5066	0.0514	85	145
PEG200DMA (Sigma-Aldrich)	Polyethylene glycol (200) dimethacrylate	330	1.08	1.4553	1.5003	0.0450	87	120
PETA (Sigma-Aldrich)	Pentaerythritol triacylate	298	1.16	1.4776	1.5134	0.0358	63	122
BPA3EODMA / SR 348C Sartomer)	Ethoxylated 3 bisphenol A dimethacrylate	496	1.12	1.5269	1.5543	0.0275	62	91
Bis-GMA (Sigma-Aldrich)	Bisphenol A glycidyl dimethacrylate	512	1.16	1.5369	1.5632	0.0263	50	55
<b>Polyester acrylates</b>								
Photomer 5429 (Cognis)	Tetrafunctional polyester acrylate oligomer	–	–	1.4561	1.4839	0.0278	100	40
Laromer 8800 (BASF)	Modified polyester acrylate	–	1.20	1.4884	1.5099	0.0216	94	63
CR UVP-215 (Croda)	Polyester acrylate	–	–	1.4946	1.5153	0.0207	91	20
CR UVP-220 (Croda)	Polyester acrylate	–	–	1.4992	1.5179	0.0187	77	45
Ebecryl 851 (UCB Chemicals)	Polyester acrylate ( $f = 2.5$ )	–	1.12	1.5071	1.5337	0.0266	42	90
Ebecryl 836 (UCB Chemicals)	Polyester hexaacrylate + 25% DPGDA	–	–	1.4920	1.5138	0.0218	63	145
<b>Epoxy acrylates</b>								
Laromer 8986 (BASF)	Modified aromatic epoxy acrylate	–	1.20	1.5059	1.5298	0.0239	45	87
CN104Y50 (Sartomer)	Bisphenol A epoxy diacrylate + 50% ethoxylated 5 pentaerythritol tetraacrylate (PPTTA)	900	–	1.5075	1.5319	0.0244	57	75
Ebecryl 605 (UCB Chemicals)	Standard Bisphenol A epoxy acrylate + 25% TPGDA	–	1.17	1.5174	1.5394	0.0219	60	79
CN104C75 (Sartomer)	Bisphenol A epoxy diacrylate + 25% TPGDA	900	–	1.5277	1.5473	0.0196	76	116
Photomer 3016 (Cognis)	Bisphenol A epoxy diacrylate	452	–	1.5305	1.5509	0.0204	56	107
Ebecryl 1608 (UCB Chemicals)	Standard Bisphenol A epoxy diacrylate + 15% propoxylated glycerol triacrylate (PPGTA)	–	1.17	1.5312	1.5483	0.0171	49	75
Photomer 3015 (Cognis)	Bisphenol A epoxy diacrylate	–	–	1.5321	1.5509	0.0188	62	39
Ebecryl 3700 (UCB Chemicals)	Standard Bisphenol A epoxy diacrylate	524	1.17	1.5454	1.5613	0.0160	44	107

– = not specified; <sup>(a)</sup>commercial data; <sup>(b)</sup>measured by FTIR spectroscopy; <sup>(c)</sup>measured by refractometry; <sup>(d)</sup>measured by DMA



**Figure 4.** Evolution of the refractive index value of commercial (meth)acrylic resins before (●) and after (○) photopolymerization ( $T = 30\text{ }^{\circ}\text{C}$  –  $I_0 = 20\text{ mW}\cdot\text{cm}^{-2}$  – double bond conversion [%] at the end of reaction is specified).

ranging from 44 to 76%). It can be also noted that, comparing the different difunctional ether acrylate resins, the higher the resin molecular mass, the lower the refractive index variation after polymerization. Regardless of ultimate double bond conversion, all these results are in accordance with the fact that the volume shrinkage is usually higher in the case of ‘small’ aliphatic molecules compared to ‘big’ aromatic ones [2].

In the case of multi-components systems, each component contributes to the refractive index value of the formulation. Thus, the refractive index of binary mixtures can be calculated by the sum of refractive index of each component weighted by its mass or molar fraction [12]. Within this framework, it is interesting to compare the materials obtained from standard Bisphenol A epoxy diacrylate (Ebecryl 3700, Ebecryl 605 and Ebecryl 1608). As expected, adding reactive diluent such as PPGDA (Ebecryl 1608) or TPGDA (Ebecryl 605) allowed reaching higher final double bond conversion (49% for Ebecryl 1608 and 60% Ebecryl 605) because of lower mechanical transition temperature ( $T_{\alpha} = 75\text{ }^{\circ}\text{C}$  for Ebecryl 1608 and  $T_{\alpha} = 79\text{ }^{\circ}\text{C}$  for Ebecryl 605) compared to the pure resin (44% and  $T_{\alpha} = 107\text{ }^{\circ}\text{C}$  for Ebecryl 3700). The consequence was a greater refractive index increase during the photopolymerization of diluted resins (0.0219 for Ebecryl 605 against 0.0160 for Ebecryl 3700). Hence, adding a reactive diluent had two effects: first, a shift of the formulation refractive index towards lower values; second, an increase in the refractive index gap ( $\Delta n$ ) resulting from the enhancement of the final double bond conversion and

consequently, higher volume shrinkage and material density.

#### 4. Conclusions

Results presented in this paper are not trivial in literature. However, these ones are indispensable both for some targeted applications and for enhancing the photopolymerization process applied to thick composite materials. For example, the only way to obtain an optically transparent composite material is that refractive indices of both filler and final photopolymerized matrix match. As well, to obtain thick homogeneous composite material, the knowledge of the UV light intensity inside the medium and its evolution requires knowing the evolution of refractive indices during the process implementation.

#### References

- [1] Bayou S., Mouzali M., Aloui F., Lecamp L., Lebaudy P.: Simulation of conversion profiles inside a thick dental material photopolymerized in the presence of nanofillers. *Polymer*, **45**, 863–870 (2013). <https://doi.org/10.1038/pj.2012.226>
- [2] Vreven J., Raskin A., Sabbagh J., Vermeersch G., Leloup G.: *Résines composites* (in French). EMC-Odontologie, 23-065-E-10 (2005).
- [3] Ferracane J. L.: Resin composite—State of the art. *Dental Materials*, **27**, 29–38 (2011). <https://doi.org/10.1016/j.dental.2010.10.020>
- [4] Liu F., Jiang X., Zhang Q., Zhu M.: Strong and bioactive dental resin composite containing poly(bis-GMA) grafted hydroxyapatite whiskers and silica nanoparticles. *Composites Science and Technology*, **101**, 86–93 (2014). <https://doi.org/10.1016/j.compscitech.2014.07.001>

- [5] Kardar P., Ebrahimi M., Bastani S.: Influence of temperature and light intensity on the photocuring process and kinetics parameters of a pigmented UV curable system. *Journal of Thermal Analysis and Calorimetry*, **118**, 541–549 (2014).  
<https://doi.org/10.1007/s10973-014-3984-z>
- [6] Macarie L., Ilia G.: Influence of pigment properties on UV-curing efficiency. *Journal of Applied Polymer Science*, **104**, 247–252 (2007).  
<https://doi.org/10.1002/app.25563>
- [7] Chartier T., Badev A., Abouliatim Y., Lebaudy P., Lecamp L.: Stereolithography process: Influence of the rheology of silica suspensions and of the medium on polymerization kinetics – Cured depth and width. *Journal of the European Ceramic Society*, **32**, 1625–1634 (2012).  
<https://doi.org/10.1016/j.jeurceramsoc.2012.01.010>
- [8] Badev A., Abouliatim Y., Chartier T., Lecamp L., Lebaudy P., Chaput C., Delage C.: Photopolymerization kinetics of a polyether acrylate in the presence of ceramic fillers used in stereolithography. *Journal of Photochemistry and Photobiology A: Chemistry*, **222**, 117–122 (2011).  
<https://doi.org/10.1016/j.jphotochem.2011.05.010>
- [9] Bae C.-J., Halloran J. W.: Integrally cored ceramic mold fabricated by ceramic stereolithography. *International Journal of Applied Ceramic Technology*, **8**, 255–262 (2011).  
<https://doi.org/10.1111/j.1744-7402.2010.02568.x>
- [10] Lee J. H., Prud'homme R. K., Aksay I. A.: Processing of organic/inorganic composites by stereolithography. *Material Research Society Symposium – Proceedings*, **625**, 165–172 (2000).  
<https://doi.org/10.1557/PROC-625-165>
- [11] Shortall A. C., Palin W. M., Burtscher P.: Refractive index mismatch and monomer reactivity influence composite curing depth. *Journal of Dental Research*, **87**, 84–88 (2008).  
<https://doi.org/10.1177/154405910808700115>
- [12] Suzuki H., Taira M., Wakasa K., Yamaki M.: Refractive-index-adjustable fillers for visible-light-cured dental resin composites: Preparation of TiO<sub>2</sub>-SiO<sub>2</sub> glass powder by the sol-gel process. *Journal of Dental Research*, **70**, 883–888 (1991).  
<https://doi.org/10.1177/00220345910700050401>
- [13] Fujita K., Nishiyama N., Nemoto K., Okada T., Ikemi Y.: Effect of base monomer's refractive index on curing depth and polymerization conversion of photo-cured resin composites. *Dental Materials Journal*, **24**, 403–408 (2005).  
<https://doi.org/10.4012/dmj.24.403>
- [14] Aloui F., Lecamp L., Lebaudy P., Burel F.: Relationships between refractive index change and light scattering during photopolymerization of acrylic composite formulations. *Journal of the European Ceramic Society*, **36**, 1805–1809 (2016).  
<https://doi.org/10.1016/j.jeurceramsoc.2016.01.033>
- [15] Castagna R., Vita F., Lucchetta D. E., Criante L., Simoni F.: Superior-performance polymeric composite materials for high-density optical data storage. *Advanced Materials*, **21**, 589–592 (2009).  
<https://doi.org/10.1002/adma.200801822>
- [16] Park S.-M., Oh C.-Y., Jo N.-J.: Fabrication and properties of glass cloth reinforced multifunctional acrylic polymer substrate. *Polymer Bulletin*, **73**, 2485–2492 (2016).  
<https://doi.org/10.1007/s00289-016-1676-5>
- [17] Meng Y., Tsai M., Schmidt G. R., Anthamatten M.: Gradient-index materials based on thiol-ene networks. *ACS Applied Materials and Interfaces*, **7**, 8601–8605 (2015).  
<https://doi.org/10.1021/acsami.5b00650>
- [18] Asuncion M. Z., Krug D. J., Abu-Seir H. W., Laine R. M.: Facile thiol-ene reactions of vinyl T<sub>10</sub>/T<sub>12</sub> silsesquioxanes for controlled refractive indices for transparent fiber glass reinforced composites. *Journal of the Ceramic Society of Japan*, **123**, 725–731 (2015).  
<https://doi.org/10.2109/jcersj2.123.725>
- [19] Aloui F., Lecamp L., Lebaudy P., Burel F.: A numerical tool for studying photopolymerization inside thick composites: Influence of optical properties on the conversion profiles for a silica/TEGDMA-BisGMA formulation. *Journal of Photochemistry and Photobiology A: Chemistry*, **356**, 418–424 (2018).  
<https://doi.org/10.1016/j.jphotochem.2018.01.023>
- [20] Matsuda T., Funae Y., Yoshida M., Yamamoto T., Takaya T.: Optical material of high refractive index resin composed of sulfur-containing aliphatic and alicyclic methacrylates. *Journal of Applied Polymer Science*, **76**, 45–49 (2000).  
[https://doi.org/10.1002/\(SICI\)1097-4628\(20000404\)76:1<45::AID-APP6>3.0.CO;2-M](https://doi.org/10.1002/(SICI)1097-4628(20000404)76:1<45::AID-APP6>3.0.CO;2-M)
- [21] Hadis M. A., Tomlins P. H., Shortall A. C., Palin W. M.: Dynamic monitoring of refractive index change through photoactive resins. *Dental Materials*, **26**, 1106–1112 (2010).  
<https://doi.org/10.1016/j.dental.2010.07.011>
- [22] Howard B., Wilson N. D., Newman S. M., Pfeifer C. S., Stansbury J. W.: Relationships between conversion, temperature and optical properties during composite photopolymerization. *Acta Biomaterialia*, **6**, 2053–2059 (2010).  
<https://doi.org/10.1016/j.actbio.2009.11.006>
- [23] Koseki K., Sakamaki H., Jeong K.-M.: *In situ* measurement of shrinkage behavior of photopolymers. *Journal of Photopolymer Science and Technology*, **26**, 567–572 (2013).  
<https://doi.org/10.2494/photopolymer.26.567>
- [24] Lecamp L., Youssef B., Bunel C., Lebaudy P.: Photoinitiated polymerization of a dimethacrylate oligomer: 1. Influence of photoinitiator concentration, temperature and light intensity. *Polymer*, **38**, 6089–6096 (1997).  
[https://doi.org/10.1016/S0032-3861\(97\)00184-5](https://doi.org/10.1016/S0032-3861(97)00184-5)
- [25] Mills N. J.: Optical properties. in 'Polymer science: A materials science handbook' (ed.: Jenkins A. D.) North-Holland Publishing, Amsterdam, Vol 1, 489–535 (1972).