

1 *Conference Proceedings Paper*

## 2 **Vanillin acrylate-based photocross-linked polymers:** 3 **synthesis and investigation of properties**

4 **Aukse Navaruckiene<sup>1</sup>, Greta Motiekaityte<sup>1</sup> and Jolita Ostrauskaite<sup>1,\*</sup>**

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7 <sup>1</sup> Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu Rd. 19,  
8 LT-50254 Kaunas, Lithuania; aukse.navaruckiene@ktu.lt (A.N.); greta.motiekaityte@ktu.edu (G.M.)

9 \* Correspondence: jolita.ostrauskaite@ktu.lt (J.O.); Tel.: +37061028625

10 **Abstract:** Cross-linked polymers were obtained by photopolymerization of vanillin derivatives  
11 (vanillin dimethacrylate and vanillin diacrylate) using ethyl(2,4,6-  
12 trimethylbenzoyl)phenylphosphinate as photoinitiator. The changes of rheological properties were  
13 examined during the curing process under ultraviolet/visible radiation. The influence of solvent,  
14 amount of photoinitiator, and vanillin derivative to cross-linked polymer properties and reaction  
15 rate was investigated.

16 **Keywords:** vanillin dimethacrylate; vanillin diacrylate; photopolymerization.

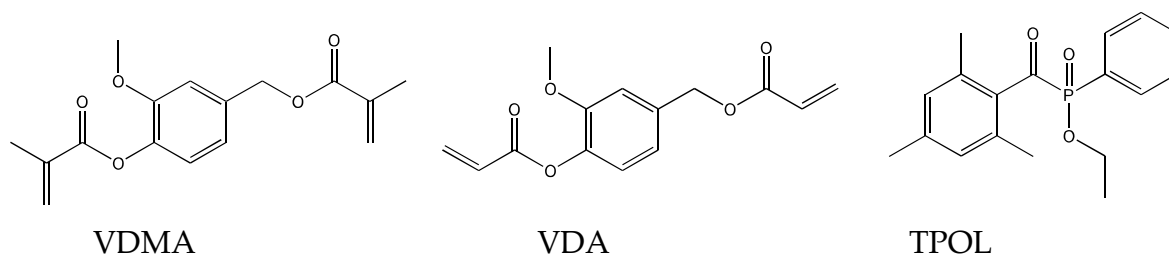
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### 18 **1. Introduction**

19 Vanillin produced by chemical modification of lignin is considered as natural vanillin and is 250  
20 times cheaper than synthetic vanillin. Due to aromatic structure it could be able to replace widely  
21 used petro-based aromatic monomers [1]. Photopolymerization engendered high interest both in  
22 academia and in industry due to the considerable practical and economic benefits. Advantages of the  
23 photopolymerization are following: high reaction speed, low energy consumption, high efficiency,  
24 low volatile organic compound emission, and the large number of applications in not only  
25 conventional areas such as coatings, inks, and adhesives, but also in high-tech domains, such as  
26 microelectronics, optoelectronics, laser imaging, stereolithography, and nanotechnology [2-3].

27 In this study, cross-linked polymers were obtained by photopolymerization of vanillin  
28 diacrylate (VDA) or vanillin dimethacrylate (VDMA) using ethyl(2,4,6-  
29 trimethylbenzoyl)phenylphosphinate (TPOL) as photoinitiator (Figure 1.). TPOL was selected due to  
30 the liquid form at room temperature and the high reaction rate [10]. Real-time photorheometry was  
31 used to evaluate the influence of selected vanillin derivative, amount of photoinitiator, and the  
32 presence of solvent to rigidity and photocross-linking rate of resulting polymers. Thermal properties  
33 were investigated by differential scanning calorimetry and thermogravimetric analysis.

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**Figure 1.** Structure of vanillin dimethacrylate (VDMA), vanillin diacrylate (VDA) and ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate (TPOL)

## 40 2. Experiments

### 41 2.1. Materials

42 Ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate (TPOL) was purchased from Fluorochem.  
 43 Vanillin diacrylate (VDA) and vanillin dimethacrylate (VDMA) were purchased from Specific  
 44 Polymers. Dichloromethane (DCM) was purchased from Reachem Slovakia. All these materials were  
 45 used as received.

### 46 2.2. Real-time photorheometry

47 UV/Vis real-time photorheometry curing tests were performed with resins containing 1 mol of  
 48 vanillin derivative (VDMA or VDA) and 1, 3 or 5 mol.% of photoinitiator (TPOL) (Table 1) on a  
 49 MCR302 rheometer from Anton Paar equipped with the plate/plate measuring system. The detailed  
 50 description can be found in a previous publication [4].

51 **Table 1.** Composition of the resins C1-C9

Resin	Vanillin derivative	Amount of photoinitiator TPOL, mol.%	Solvent
C1	VDA	1	-
C2	VDA	1	DCM
C3	VDMA	1	DCM
C4	VDA	3	-
C5	VDA	3	DCM
C6	VDMA	3	DCM
C7	VDA	5	-
C8	VDA	5	DCM
C9	VDMA	5	DCM

### 52 2.3. Preparation of cross-linked polymer specimens

53 The resins, containing vanillin derivative (VDA or VDMA), a minimal amount of DCM and 1, 3  
 54 or 5 mol.% of TPOL were stirred at room temperature (25 °C) with a magnetic stirrer until  
 55 homogenous phase was reached. Then homogenous resins were poured into a Teflon mold and cured  
 56 for 1-4 min under the Helios Italquartz UV lamp (model GR.E 500 W) with UV/Vis light at intensity  
 57 of 310 mW/cm<sup>2</sup>.

### 58 2.4. Characterization of thermal properties

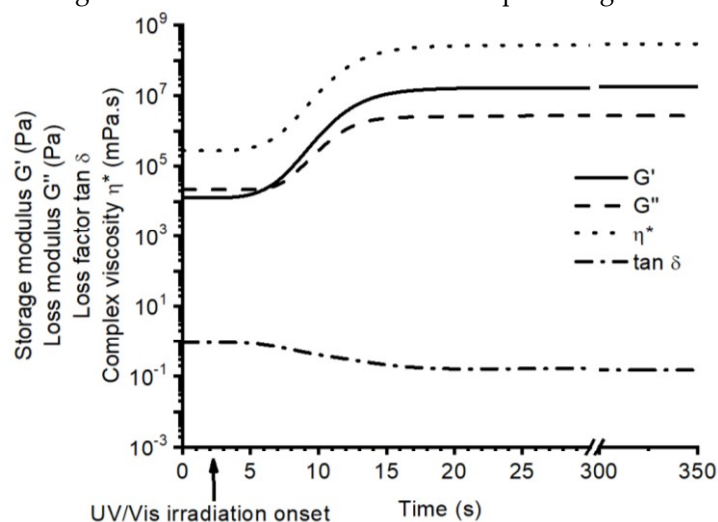
59 Differential scanning calorimetry (DSC) measurements were performed on a DSC 8500  
 60 apparatus (Perkin Elmer, Llantrisant, UK), thermogravimetical analysis (TGA) was performed on

61 a TGA 4000 apparatus (Perkin Elmer, Llantrisant, UK). The detailed description can be found in a  
 62 previous publication [5].

### 63 3. Results

#### 64 3.1. Monitoring of photocross-linking kinetics by real-time photorheometry

65 Due to illumination of the photosensitive reaction mixture,  $G'$ ,  $G''$ , and  $\eta$  begin to increase  
 66 rapidly due to the growth of polymer chain and the formation of polymer network. As the  
 67 photopolymerization proceeds,  $G'$  increases faster and acquires higher values than  $G''$ . Such a sudden  
 68 increase in  $G'$  occurs due to the formation of polymer network, during which a high-viscosity  
 69 Newtonian fluid turns into a solid elastic material. This phase transition is characterized by the point  
 70 of intersection of  $G'$  and  $G''$ , which is called a gel point. Subsequently,  $G'$  and  $G''$  continue to increase  
 71 as the reaction proceeds. Lower values of  $G''$  compared to  $G'$  indicate higher elastic properties of the  
 72 formed polymer network. The decrease in  $\tan\delta$  during the crosslinking reaction indicates that the  
 73 polymer becomes a solid elastic body. Figure 2 shows the evolution of storage modulus  $G'$ , loss  
 74 modulus  $G''$ , loss factor  $\tan\delta$ , and complex viscosity  $\eta^*$  of the VDA-based resin C4 during UV/Vis  
 75 irradiation. [6]. The rheological characteristics of all tested samples are given in Table 2.



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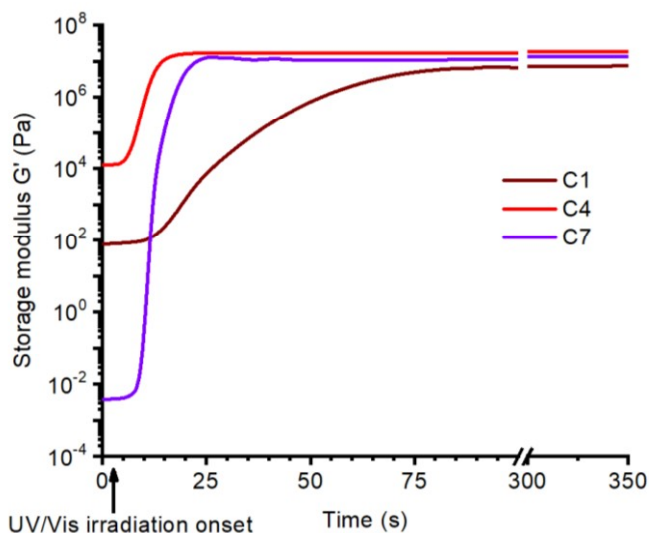
77 **Figure 2.** Dependencies of storage modulus  $G'$ , loss modulus  $G''$ , loss factor  $\tan\delta$ , and complex  
 78 viscosity  $\eta^*$  of the resin C4 on irradiation time

79 **Table 2.** Rheological characteristics of the resins C1-C9

Resin	Storage modulus $G'$ , MPa	Complex viscosity $\eta^*$ , mPa.s	Loss modulus $G''$ , MPa	Gel point <sup>a</sup> $t_{gel}$ , s
C1	7.35	0.15	6.34	10
C2	13.40	0.22	2.35	20
C3	13.00	0.21	1.65	6
C4	18.10	0.29	2.70	6
C5	11.30	0.18	1.64	12
C6	18.20	0.29	2.94	5
C7	13.30	0.23	5.78	10
C8	14.50	0.23	2.02	14
C9	19.80	0.32	3.36	6

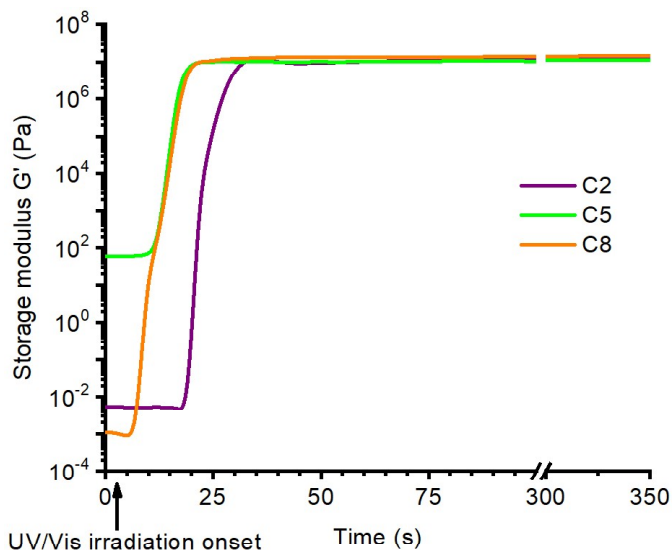
80 a- calculated from the UV/Vis irradiation onset.

81 Comparing the shape of the storage modulus curves of the resins with different concentration of  
 82 photoinitiator, the highest final rigidity and the fastest photocross-linking was demonstrated by the  
 83 resin C4 with 3 mol.% of TPOL in the VDA-based resins without solvent series (C1, C4 and C7) (Figure  
 84 3.).



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 86 **Figure 3.** Dependencies of storage modulus  $G'$  of the VDA-based resins C1, C4 and C7 with different  
 87 amount of photoinitiator on irradiation time

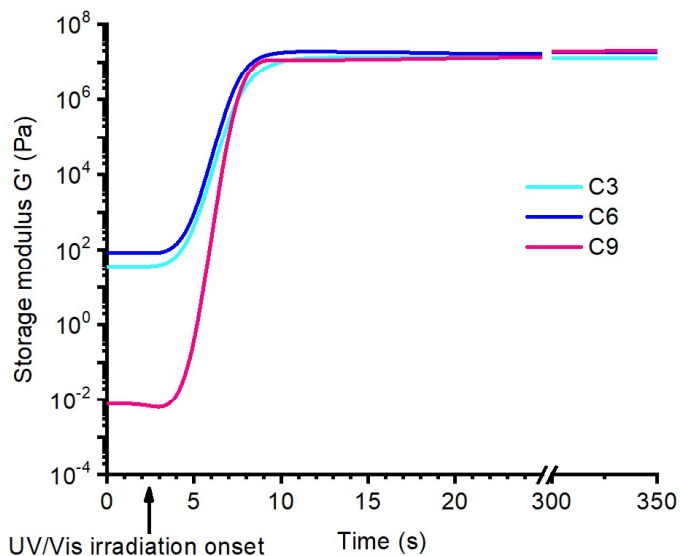
88 The presence of solvent had the higher influence to the photocross-linking rate than the concentration  
 89 of photoinitiator. In VDA-based resins with solvent series (C2, C5 and C8), the photocross-linking  
 90 rate of resins with 3 mol.% and 5 mol.% of TPOL (C5 and C8 respectively) was similar and faster than  
 91 that of the resin C2 with 1 mol.% of TPOL, although the more rigid polymer was obtained from the  
 92 resin C8 (Figure 4.).



93  
 94 **Figure 4.** Dependencies of storage modulus  $G'$  of the VDA-based resins C2, C5 and C8 with different  
 95 amount of photoinitiator on irradiation time

96 In VDMA-based resins with solvent series (C3, C6 and C9), the photocross-linking rate did not  
 97 depend on the concentration of TPOL, although the more rigid polymer was obtained from the resin

98 C9 with 5 mol.% of TPOL (Figure 5). Comparing the gel points ( $t_{gel}$ ) of the resins (Table 2), the  $t_{gel}$  was  
 99 reached the fastest when 3 mol.% of photoinitiator was used in the case of all resin series.



100 UV/Vis irradiation onset Time (s)

101 **Figure 5.** Dependencies of storage modulus  $G'$  of the VDMA-based resins C3, C6 and C9 with  
 102 different amount of photoinitiator on irradiation time

103 *3.2. Thermal properties of photocross-linked polymers*

104 Thermal characteristics of the photocross-linked polymers C4-C6 were obtained DSC and TGA  
 105 experiments. Vanillin-based polymers are amorphous materials, only the glass transition  
 106 temperature is visible in DSC curves. Polymer C5 demonstrated the lowest glass transition  
 107 temperature (63 °C). Polymers C4 and C6 demonstrated similar glass transition temperature 87 °C  
 108 and 86 °C, respectively. The glass transition temperatures of obtained vanillin-based polymers are  
 109 similar to the acrylate resins based on natural phenolics, which were presented as candidate materials  
 110 for stereolithography (79 °C) [7].

111 Thermogravimetical analysis was used to investigate thermal decomposition of vanillin-based  
 112 polymers. The temperature of 10 % weight loss ( $T_{dec.-10\%}$ ) was the highest for VDA-based polymer C4  
 113 (350 °C). C5 and C6 polymers, which were prepared with DCM, both demonstrated lower  
 114 temperature of 10 % weight loss (330 °C and 340 °C, respectively).  $T_{dec.-10\%}$  of obtained vanillin-based  
 115 polymers is similar or even slightly higher than  $T_{dec.-10\%}$  of some acrylated epoxidized soybean oil  
 116 based polymers (297 - 356 °C) tested in optical 3D printing [8].

117 **4. Conclusions**

118 Novel vanillin acrylate-based cross-linked polymers were obtained by the photopolymerization of vanillin  
 119 diacrylate and vanillin dimethacrylate using ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate as photoinitiator.  
 120 Investigation of photopolymerization kinetics revealed that no use of solvent and usage of 3 mol.% of ethyl(2,4,6-  
 121 trimethylbenzoyl)phenylphosphinate increased polymer rigidity. Photopolymerization was the fastest when 3  
 122 mol.% of photoinitiator were used. Vanillin dimethacrylate-based systems showed lower values of gel point and  
 123 polymerized faster than vanillin diacrylate-based systems. Polymers with the fragments of vanillin diacrylate  
 124 without solvent performed higher values of thermal stability. The designed vanillin-based compositions could  
 125 be used as photosensitive resins in optical 3D printing.

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128 **Author Contributions:** J.O., A.N. and G.M. conceived and designed the experiments, analyzed the data; A.N.  
 129 performed all experiments and characterizations.

130 **Conflicts of Interest:** The authors declare no conflict of interest.

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