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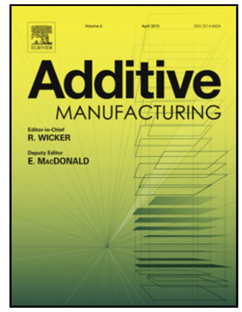

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Multi-branched Benzylidene Ketone based Photoinitiators for Multiphoton Fabrication

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ABSTRACT: In this article, we report the synthesis of a series of multi-branched benzylidene (BI) ketone-based photo-initiators for two-photon polymerisation based 3D printing/additive manufacturing. Resins prepared by the addition of 1 wt.% of these initiators were processed in a commercial 2 photon polymerisation system to fabricate 3D woodpile structures, the qualities of which were examined to determine the efficiencies of the initiators. The results showed that compared to commercial initiator Irgacure 369, the four-branched initiator 4-BI exhibited excellent performance with higher writing speeds and broader ideal processing windows. The successful fabrication of complex 3D structures at high writing speeds (up to 100 mm/s) indicated that the four-branched initiator 4-BI could potentially increase the fabrication efficiency and hence become a promising initiator for two-photon polymerisation.

1. INTRODUCTION

Since its inception, two-photon induced photo-polymerisation (TPIP) has been developed towards a manufacturing process that can produce additively manufactured (or 3D printed) structures on nano length scales[1]. This is attractive – 3D printing or additive manufacturing (AM) is a manufacturing method that seeks to avoid traditional manufacturing techniques that are either subtractive (i.e. machining and ablation) or formative (i.e. moulding and casting), and in doing so leverages considerable benefits in terms of design freedom[2,3,4,5,6]. To date, AM is able to fabricate on the super-micron scale[3,7], but there are significant benefits to also being able to tailor function on the nanoscale, e.g., being able to manufacture on lengths scales that are important for cellular function, or for interacting with the visible part of the electromagnetic spectrum[8,9]. TPIP achieves this level of resolution by employing a two-photon absorption (TPA) procedure, a non-linear process requiring two photons to breach the energy gap between an allowed excited state and the ground state[10]. This non-linearity results in a threshold intensity that induces a photochemical reaction and this can be tailored spatially through the sculpting of the incident beam profile to achieve nanoscale fabrication[11]. For those aiming to manufacture, this conveys advantages of excellent spatial control with high resolution in the sub-micrometer range[12,13]. Moreover, compared to UV light, the long wavelength excitation source (~780 nm) enables deeper penetration into the resin[14] as well as a reduction in the number of side reactions[1,11]. These advantages have resulted in TPIP being exploited in a wide range of applications, including three-dimensional (3D) microfabrication[15], biological