initiators and results in free radical. Then they react with photo curable macromers giving rise to reactive species that could take part in propagation. Stepwise growth by crosslinking happens during propagation. The termination step is characterized by the end of the crosslinking in the 3D-polymeric network (Ifkovits et al. 2007).

Photo-polymerization has been a crosslinking technique with several advantages, including low energy and rapid reactions under mild conditions. Photo-polymerisable hydrogels have been exploited for a decade in biomedical and pharmaceutical applications, mostly in tissue engineering (Nguyen et al. 2002; Ifkovits and Burdick 2007). Photo-crosslinked systems can be formulated from aqueous solutions of polymers/monomers containing photo-sensitive molecules and a catalyst upon exposure to an external irradiation source such as ultraviolet (UV) or visible light, thus forming free radicals and catalysing the polymerization. Polymers used for these reactions usually have unsaturated groups for example methacrylate or acrylate groups, which undergoes rapid polymerization in the presence of light irradiation. This approach allows for the spatial control of the cross-linked network. Moreover, the gelation rate can also be controlled timely; resulting in the formation of patterned structured hydrogels for specific applications. Alsberg et al. 2001 introduced a biodegradable photo-crosslinked hydrogel based on heparin/alginate for affinity-based growth factors delivery (Jeon et al. 2011). Different growth factors such as FGF-2, VEGF, TGF-b1 and BMP-2 were successfully released over three weeks in a sustained manner, which was attributed to the strong affinity interaction between heparin and the growth factor. Subsequently released BMP-2 and VEGF were examined for their period of bioactivity, i.e., 2 and 3 weeks, respectively.

Click chemistry

Generally, the term "click" chemistry is being defined by Sharpless and coworkers as certain reaction types that have high efficiency, excellent specificity, bioorthogonality and mild reaction conditions (Kold et al. 2001). Click chemistry has played a significant role in polymer synthesis and bio-conjugation as a flexible and efficient method to connect functionalized molecules. Click chemistry has been a great interest in the fabrication of hydrogels, nanogels and microgels as an emerging platform for tissue engineering and drug delivery. Typically, a wide and diverse range of reactions, including Cu(I) catalyzed alkyne-azide cycloaddition (CuAAc) reactions, catalyst-free alkyne-azide coupling reactions, Diels-Alder cycloaddition, Radical-mediated thiol-Michael reactions and Schiff's base reactions, could be considered to be 'click' chemistry (Fig. 3).

Thiol-based Michael reactions

Michael reaction refers to the nucleophilic addition of a nucleophile to a α, β-unsaturated carbonyl compound. Particularly, nucleophile components are thiol- and amine-bearing molecules, whereas unsaturated carbonyl components are commonly associated with acrylate, methacrylate and vinyl sulfone groups (Fig. 4). The advantages of Michael reactions are: mild conditions required, controllable reaction rate, high chemical yield