Chapter 13
Designing Self-Healing Polymers by Atom Transfer Radical Polymerization and Click Chemistry

Bhaskar Jyoti Saikia, Dhaneswar Das, Pronob Gogoi, and Swapan Kumar Dolui

Abstract The development of smart self-healing polymeric materials and composites has been the subject of a tremendous amount of research over last few years. When self-healing materials are mechanically damaged, either internally (via crack formation) or externally (by scratching), they have the ability of restoring their original strength and recovering their inherent properties. For polymers to exhibit such a healing ability, they must contain some functionality which will either rebound among themselves or have the ability of coupling with other functionalities. Preparation of such multifunctional and well-defined macromolecules requires a smart selection of a controlled polymerization technique in combination with appropriate coupling reactions. Among all the polymerization techniques introduced so far, atom transfer radical polymerization (ATRP) is the most versatile owing to its exceptional properties like preparation of polymer with predetermined molecular weight, narrow polydispersity index, predetermined chain-end functionality, and tunable architecture. Click chemistry is an extremely powerful coupling approach which in combination with ATRP can be used for generation of polymers with almost all of the desired properties. In this chapter, an overview on the use of ATRP and click chemistry for polymerization of various "clickable" monomers using "clickable" ATRP initiators is provided along with other post-polymerization modification strategies that can be used to construct macromolecules with self-healing ability.

Keywords Self-healing polymers • ATRP • Click chemistry

B.J. Saikia • D. Das • P. Gogoi • S.K. Dolui (✉)
Department of Chemical Sciences, Tezpur University, Napaam, Assam, India
e-mail: swapandolui@gmail.com

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13.1 Introduction

Inspired by nature's most remarkable features of self-repairing, the development of self-healing polymeric materials has been a subject on the frontier of research over the last decade [1–3]. Presently humanity is in an age of plastic. Polymers and their composites are used in almost every material used by modern society. However, these materials are susceptible to damage which is induced by chemical, mechanical, UV radiation, thermal, or a combination of these factors [4]. Whenever these polymeric materials become damaged, only a few methods are available to extend their service life. Manual repairing methods are insufficient in restoring the original properties of the material and require continuous monitoring when implementing. However, it is believed that a vast majority of structural failure results from the propagation of initial microcracks. Eventually if repairs can be made at the micro-level, the lifetime of the materials can be significantly enhanced. Currently, development of automatic or self-healing materials is of prime importance where it can self-repair itself immediately after even invisible microcracks are formed. Self-healing materials when damaged mechanically, either externally or internally, have the ability of healing the damage automatically, restoring its original strength. These smart polymers are gaining wide appeal in various applications such as biomedicine, electronics, paints and surface coatings, robotics, etc. Encapsulation of monomers/catalysts to polymer matrix, dynamic covalent bond formation, and supramolecular self-assembly are the prevailing adopted strategies for preparing self-healing polymers [3, 5–11]. Among various approaches investigated, in order to attain polymers exhibiting such behavior, ATRP and click chemistry are the most versatile means for tailoring the functionality of a polymer toward effective self-healing [12–15]. This chapter is based on the progress made in the methods of synthesis for self-healing polymers by ATRP and click chemistry while also providing a comprehensive discussion of click chemistry approaches to generate self-healing polymers.

13.2 Application of ATRP for Designing Self-Healing Polymers

At present, functional polymers with complex architecture are of considerable interest due to their wide range of applications, beginning with structural all the way to electronic applications. ATRP is the most versatile controlled radical polymerization technique, as it furnishes the simplest route in the design and synthesis of a large variety of well-defined polymers with predetermined molecular weight, narrow molecular weight distribution, and high degree of chain-end functionalities [16–19]. The role of ATRP in the synthesis of functional polymers makes it an exceptionally useful polymerization technique compared to ionic polymerization techniques. It has been effectively applied in the preparation of polymers with precisely controlled

functionalities, topologies, and compositions [20]. This broadens the range of monomers that can be polymerized or copolymerized via ATRP and provides the ability for the straightforward introduction of various functionalities into a polymer structure. In general, there are four major strategies for the synthesis of telechelic polymers with functional groups via ATRP:

1. By using functional initiators
2. Substitution of the terminal halogen atom with nucleophile
3. Polymerization of functional monomers
4. Polymerization of "protected" monomers, followed by post-polymerization chemical transformations

While using the first two approaches, chain-end-functionalized polymers can be harvested as the last two methods yield polymers with multiple functionalities along their backbone. Therefore, it is very convenient to apply ATRP when designing self-healing polymers as healing requires special functionalities within the polymers; typically it is nearly impossible to introduce a moiety into the polymer's backbone or chain end via other polymerization techniques.

Although numerous methods are currently available for the design of self-healing polymers and polymer composites, focus will be placed upon the strategies set forth by ATRP and click chemistry. There are three major categories of self-healing polymers or composites which can be prepared by ATRP [21]:

1. Automatic one-component self-healing polymers
2. Self-healing by semi-encapsulation methods
3. Self-healing by encapsulation method

An illustration of all the above processes is shown in Fig. 13.1.

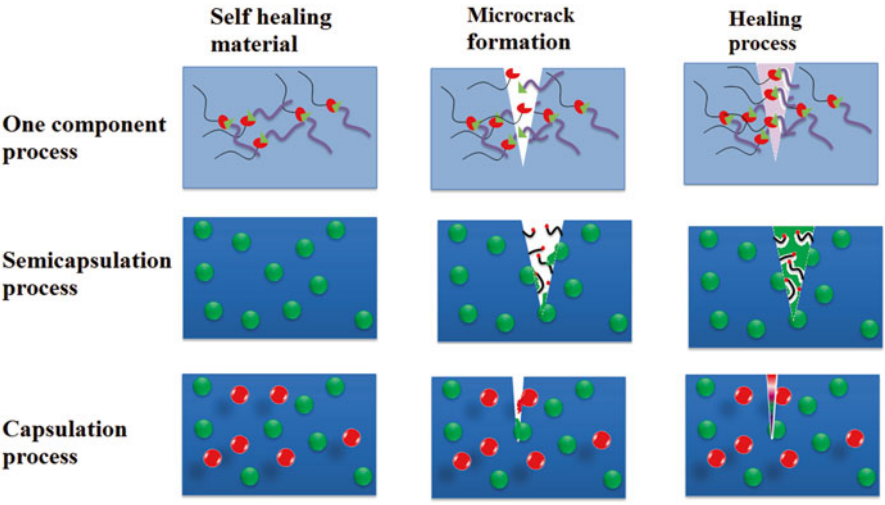


Fig. 13.1 Various approaches for synthesis of self-healing polymers

13.2.1 Automatic One-Component Self-Healing Polymers

The development of polymeric materials that automatically repair themselves after mechanical damage would significantly improve the safety, lifetime, energy efficiency, and environmental impact of these materials [22–24]. Most approaches to activating self-healing materials require an external stimulus like energy, solvent, healing agents, or plasticizers. Intrinsic self-healing materials utilize reversible chemical bonds (non-covalent and covalent) which allows for the design of single-component self-healing materials. Intrinsic self-healing mechanisms can be classified into the following two categories [21]:

1. Self-healing by reversible non-covalent bond formation
2. Self-healing by covalent bond formation

ATRP can be successfully applied in the design of all of the above categories of intrinsic self-healing polymers, as it is the most flexible polymerization method in regard to functionality and architecture.

13.2.2 ATRP for Designing Reversible Non-covalent Bond-Forming Material

The main advantage of self-healing polymers based on non-covalent bond formation is that they are reversible which allows them to heal themselves repeatedly in the same place; therefore, the recovery of the material's properties is inherent to the material's abilities. This type of polymer employs various non-covalent bonds such as hydrogen bonding, ionomers, π–π stacking, and others [25–27] to form a supramolecular network. While weak when singled out, the collaborative effort put forth by a group of these bonds creates a dynamic load-bearing structure at ambient temperature, thus enabling autonomic damage healing to take place. However, the molecular dynamics of these networks need a great deal of plasticization, as well as the single-phase dynamic assembly of small oligomers. As such, this technique can only be utilized in low-modulus rubber purposes. A balance between dynamic healing and mechanical stiffness properties is necessary when designing supramolecular systems. Intense relationships between the two produce an unyielding but less dynamic network while a weak relationship produces a soft yet dynamically healing system [28]. ATRP can be successfully applied to design a single-phase dynamic polymer chain that contains both stiff and flexible moieties in the same molecule (Fig. 13.2).

Thus a useful method for developing self-healing polymers is by incorporating reversible non-covalent hydrogen-bonding moieties into the polymer structure. Yulin Chen and his coworkers [28] have demonstrated a novel multiphase design methodology for an autonomic responsive healing system that can impart crucial mechanical properties (e.g., high modulus, high elasticity, and toughness) via

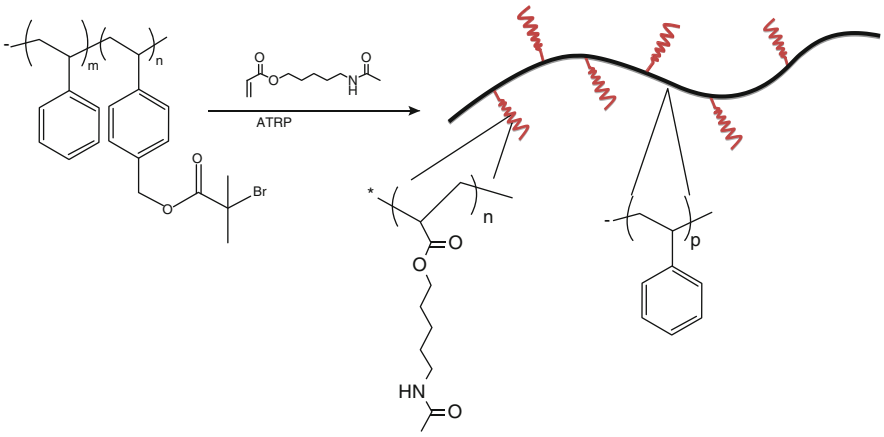
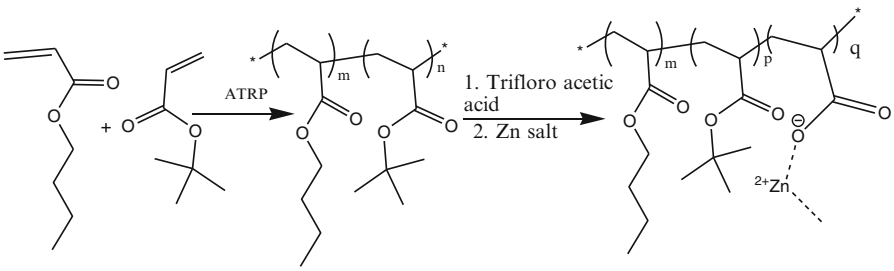


Fig. 13.2 An intrinsic self-healing polymer with a stiff backbone of polystyrene along with flexible side chain [28]

hydrogen bonding and ATRP. The research team was able to repair, on demand and without any external intervention, a single-component solid material.

π–π interactions are associated with the interaction between the π-orbitals of a molecular system. Self-healing materials based on aromatic π–π stacking interactions can be synthesized combining π-electron-rich (e.g., pyrenyl) and π-electron-poor (e.g., diimide) moieties in the same polymer chain [29]. π–π stacking interactions can also be achieved by preparing end-capped π-electron-deficient groups with other π-electron-rich aromatic backbones [30]. Since end-capped polymers can be achieved by using relevant initiators via ATRP, it is a useful method in the preparation of self-healing polymers with π–π stacking. Post-polymerization modification of polymer chains prepared by ATRP or the preparation of various shapes of polymers such as heteroarmed stars or brushes can also fulfill these requirements. Heteroarmed star polymers designed by ATRP are especially advantageous when designing a self-healing polymer with substantial π–π interactions. The use of dynamic bonds in self-healing polymeric systems allows for the restoration of the chemical structure and mechanical properties multiple times. In this respect, the use of ionomers represents a promising approach. Ionomeric copolymers are a class of polymer which contains ionic segments (normally not more than 20 %) that can form clusters that act as reversible cross-links [30]. These clusters can be activated by external stimuli such as temperature or ultraviolet (UV) irradiation. Since the formation of the clusters is reversible, multiple local healing events are possible. The heat generated during projectile damage can act as the trigger for a self-healing event when using this type of polymer. Direct ATRP is less applicable when synthesizing this type of polymer, but post-polymerization modification methods can be employed. For example N. Hohlbein et al. [31] reported a model system based on the copolymers of n-butyl acrylate and a varying fraction of t-butyl acrylate which was prepared by ATRP with adjustable molecular weight and a



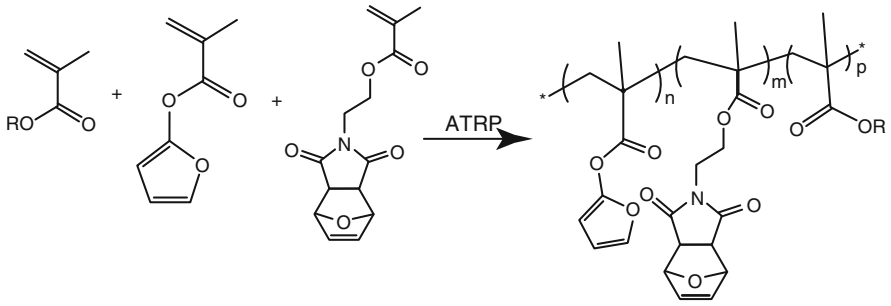
Scheme 13.1 Schematic representation of formation of ionomers by ATRP

narrow molecular weight distribution. Carboxylic acid moieties were formed by hydrolysis of the t-butyl acrylate moiety that was subsequently neutralized with basic sodium, zinc, or cobalt salts to produce the corresponding ionomer (Scheme 13.1). Carboxylated NBR was transferred to these ionomeric elastomers. For synthesis of composites that are activated via localized heating, cobalt, magnetite, and cobalt ferrite nanoparticles were incorporated in different contents into the model copolymer and NBR matrices, respectively, resulting in highly efficient stimulated self-healing material.

13.2.3 Self-Healing by Covalent Bond Formation

Covalent bond formation is undoubtedly an efficient healing technique. Numerous methods are available under this category and can be subdivided into reversible and irreversible methods. Reversible methods, like the Diels–Alder/retro-Diels–Alder (DA/r-DA) reactions or polycondensations provide the opportunity for multiple healing cycles, while irreversible methods, like the microcapsule-based concept, epoxides, or various click approaches cannot heal once an area is damaged a second time. Single-component intrinsic self-healing polymers with reversible bond formation can be easily synthesized by ATRP. DA healing reactions are the most popular for this purpose [32]. Acrylic-based one-component polymer systems can be easily synthesized, containing both binding units for the DA reaction (i.e., maleimide and the furan moiety) along with relevant comonomers to tune the mechanical and thermal properties (Scheme 13.2). The ATRP of maleimide methacrylate (MIMA) and furfuryl methacrylate (FMA) along with different acrylic polymers can be utilized to synthesize well-defined functional terpolymers, which could be cross-linked via subsequent thermal treatments [33].

Similarly, ATRP can be used for copolymerization of functional monomers either directly or by post-polymerization modification, yielding one-component, reversible, covalent bond-forming polymers. It is however generally not possible to synthesize one-component self-healing polymers with *irreversible covalent* bond formation by ATRP as most ATRP processes require elevated temperatures where cross-linking reactions are most likely to occur.



Scheme 13.2 Schematic representation of synthesis of intrinsic DA/r-DA self-healing polymer by ATRP

13.2.4 Self-Healing by Semi-encapsulation Methods

Semi-encapsulation methods are those in which healing agents are encapsulated in nano- or microcapsules which are homogenously dispersed in the polymer matrix. Most of these methods are intrinsic healing methods as they do not require external stimuli. Presently microcapsules have been widely used for the fabrication of self-healing polymers and polymeric composites [34–37].

The mechanism is based on the fact that microcapsules containing a healing agent are pre-embedded in the polymer matrix. When these microcapsules are ruptured upon cracking, they release the reparative substance into the cracked planes, which is then polymerized and re-bond the damaged portions. Development within this methodology offers considerable potential toward extending the service life of structural materials and saving on maintenance costs. Poly(urea–formaldehyde)-walled microcapsules containing dicyclopentadiene [38], poly(urea–formaldehyde)-walled microcapsules containing epoxy [39], melamine–formaldehyde resin-walled microcapsules containing dicyclopentadiene [40], and many others are most extensively used for this purpose. The healing agent may be a monomer, cross-linker, or oligomer where the polymer matrix may be reactive toward the encapsulated agents.

Formation of microcracks in the polymers also breaks these capsules, leaching out the healing agents to the cracks. ATRP can be extensively used for the preparation of a reactive thermoplastic matrix. Since polymers prepared by ATRP retain their "living" characteristics, this property alone can provide the self-healing nature required. Living polymerization is a polymerization process in which the chain transfer and termination process is removed [41]. Because the resultant polymer carries living ends, chain growth is always allowed as long as reactive monomers are available. It is therefore a popular method for synthesizing block copolymers since the polymer can be prepared in stages, each of which contains a different monomer. Due to this interesting characteristic of living polymerization, a self-healing polymer can be prepared with a microencapsulated monomer (healing agent) with a living polymer matrix.

Owing to the infinitely long lives of the molecule chain ends of the matrix, as soon as the monomer is released from the spheres as a result of crack initiation or propagation, the polymerization process of the healing agent (monomers) will begin at ambient temperature wherever the monomer meets the matrix. Formation of covalent bonds as a result of copolymerization through the healing process restores the original strength (sometimes better depending upon the type of encapsulated monomer) back to the polymer. The newly formed macromolecules, which are covalently attached to the interface, fill the interstitial space of cracks and fuse with the matrix. This is a very good way to achieve multiple healing events.

13.2.5 Self-Healing by Encapsulation Method

The encapsulation method is a dual capsule self-healing system in which two different reactive components are encapsulated separately and dispersed in the thermoset or thermoplastic polymer matrix that will require healing [23].The two components must have sufficient stability in the service life of the base polymer or composite and high reactivity when exposed to one another. It is the oldest and most widely used method for designing self-healing polymers. In regard to mass production and application popularity, the synthesis approach based upon binary microcapsules containing liquid healing agent is fairly promising. The ATRP-based encapsulation method utilizes two low-molecular-weight polymers having reactive functionalities as healing agents. Azide–alkyne cycloaddition, Diels–Alder reaction, thiol–ene reaction, thiol–yne reaction, and so forth can be utilized in the healing reaction (to be discussed later) if one microcapsule contains the first functionality and the other microcapsule contains the second functionality. Low-molecular-weight star-shaped polymers are especially beneficial in this capacity as they have low viscosity and very high density functionality.

13.3 Click Chemistry

Thought of as an environmentally friendly alternative, click chemistry deals with the instantaneous nearly 100 % efficient creations of molecules without by-product all while utilizing mild reaction conditions.

Sharpless and coworkers [42] defined the reaction as being large in ability, being simple to complete, having no exotic reagents required, and being unaffected by oxygen and water. There are even multiple circumstances where water acts as the ideal reaction solvent, producing at the highest amounts and fastest times. With purification and analysis avoiding harsh solvents and chromatographs, click chemistry, though not as easily definable as a reaction, describes a methodology in the creation of products in such a way that mimics nature while creating materials through the combination of tinier building blocks.

In summary, desirable click chemistry reaction would have the following key characteristics [42]: modular, large scope, high yielding, has inconsequential by-product production, stereospecific, physiologically stable, has high atom economy, and exhibits a large thermodynamic driving force (>84 kJ/mol) in order to favor a reaction with a single reaction product. Furthermore, the process would preferably have the following restrictions: possesses simple reaction conditions, requires no exotic materials or reagents, uses only benign or easily removable solvents, and provides simple product isolation via non-chromatographic methods.

The potential of click chemistry for material synthesis has been increasingly recognized and has already resulted in the growth of a wide range of smart materials. Owing to their high selectivity, high yields, and tolerance toward a wide range of functional groups and reaction conditions, click reactions have recently attracted increased attention in polymer synthesis in addition to polymer modification [43–48]. Owing to their many promising benefits, click chemistry has been exclusively used as a cross-linking reaction in the design of self-healing polymers, providing highly efficient healing. Among various click reactions, DA/r-DA, azide–alkyne cycloaddition, and thiol–ene/yne click reactions are broadly applicable in the field of polymer chemistry as well as in the design of self-healing polymers. An overview of these click reactions used for designing self-healing polymers is discussed below.

13.3.1 Diels–Alder (and Retro-Diels–Alder) Click Reaction

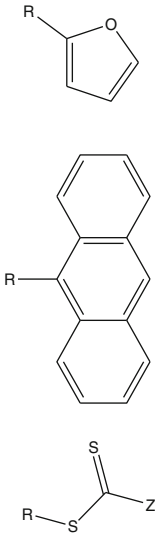
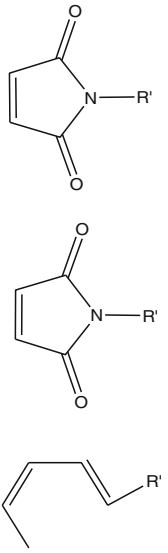
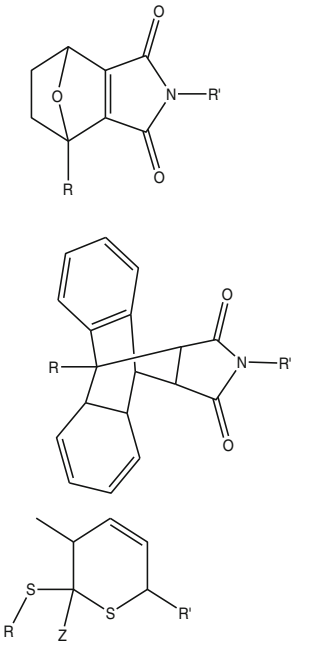
The most known reaction employed in the creation of intrinsic self-healing materials is the Diels–Alder (DA) reaction. DA reaction meets most of the requirements needed to be a click reaction. A stable cyclohexene adduct is formed from the 4 + 2 cycloaddition reaction between electron-rich dienes (furan and its derivatives, 1,3-cyclopentadiene and its derivatives, etc.) and electron-poor dienophiles (maleic acid and its derivatives, vinyl ketone, etc.) (Table 13.1).This reaction has become one of the most frequently used reactions in polymer science as it has extremely low energy requirements to form a cyclohexene ring while simultaneously allowing the formation and functionalization of numerous molecules. The general mechanism of DA/r-DA reaction is given in Scheme 13.3.

DA click reaction can be utilized for self-healing materials in the following ways:

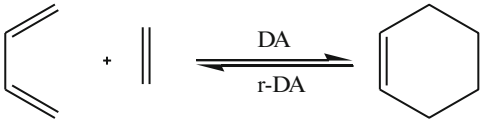
(a) Using telechelic polymers with DA functionality

The DA click reaction can be applied in the synthesis of telechelic polymers. Telechelic polymers are those macromolecules which contain reactive end groups that have the capacity to enter into further polymerizations or other reactions. A simple matrix of telechelic polymers with DA functionality or a mixture of two compatible polymers with DA functionality can act as a thermally triggered self-healing polymer (Fig. 13.3).

Table 13.1 Selected DA reaction for synthesis of self-healing polymers

Reagent A	Reagent B	Mechanism	Adduct
		[4+2] r-DA	
		[4+2] DA	
		[4+2] hetero-DA	

Scheme 13.3 General mechanism of DA/r-DA reaction



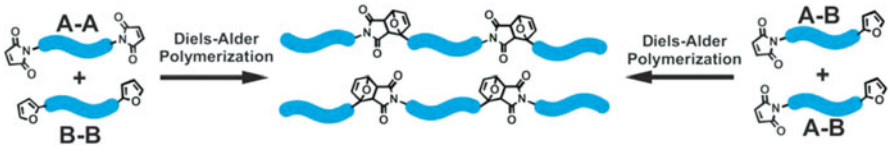


Fig. 13.3 Coupling process of a telechelic polymer with DA functionality (reprinted with permission from [31])

(b) Using bifunctional polymers

In this approach, two monomers, one carrying a diene and another carrying a dienophile group, are reacted to yield a cross-linked copolymer (reaction scheme same as Scheme 13.1). Healing of any crack formation can be achieved by heating the polymer above the temperature required for a reversible DA reaction to occur. The heat causes a partial disconnection of the polymer chains and increases the mobility of individual chains. Upon cooling, new DA bonds are formed and the chains become cross-linked again, thus healing the crack (Fig. 13.4).

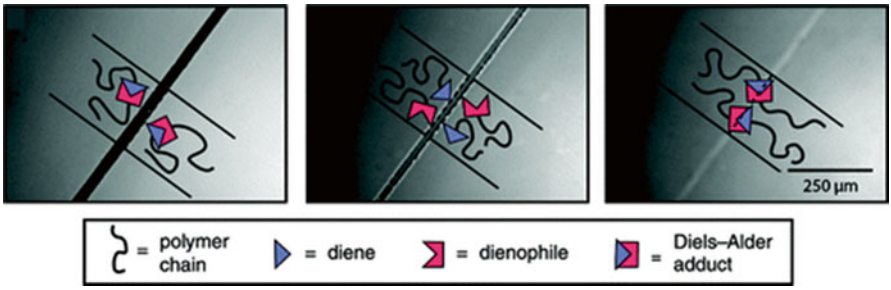
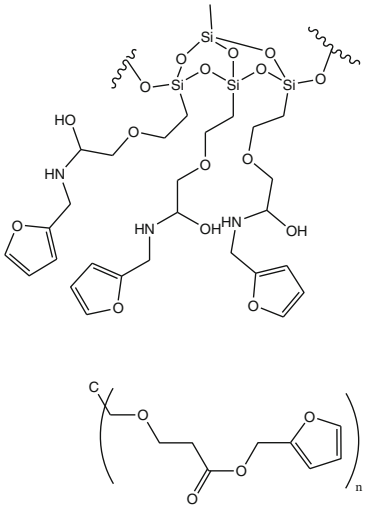
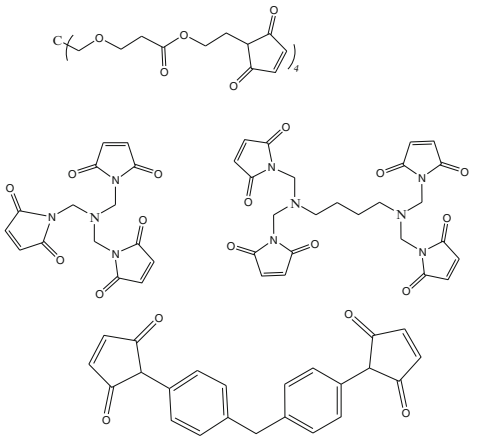
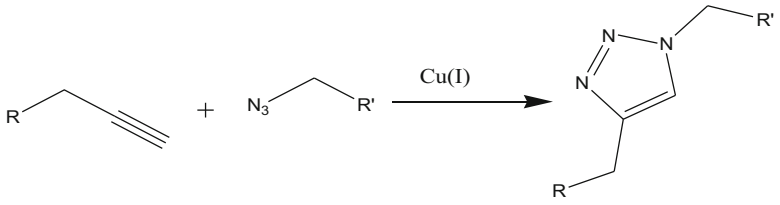


Fig. 13.4 Thermally reversible self-healing process via DA/r-DA clicks (reprinted with permission from [47])

(c) Encapsulation method

When employing the encapsulation method, both thermoplastic and thermosetting plastics as well as their composites can be fashioned into self-healable materials using the binary capsule system via DA/r-DA. This approach requires one capsule having a multifunctional diene and another capsule having a multifunctional dienophile. The primary requirement is that the reagents must crosslink so as to generate a solid mass so that upon crack formation, they can act as internal glue. Some examples of such diene and dienophile reagent systems are given below:

Multifunctional dienes	Multifunctional dienophiles
	



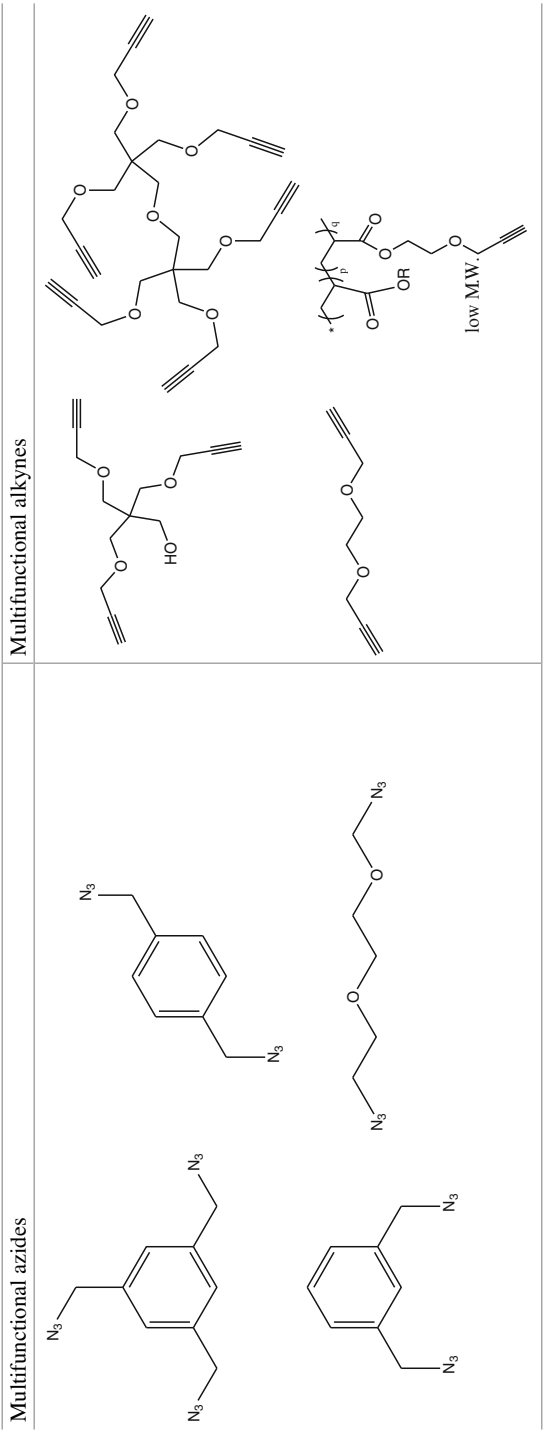
Scheme 13.4 General mechanism of CuAAC

13.3.2 Cu (I)-Catalyzed Azide–Alkyne Cycloaddition (CuAAC)

Although the DA/r-DA reaction discussed above is a valuable tool for tailoring self-healing materials, in most of these cases, the underlying DA reactions require temperatures significantly higher than room temperature, often at 80–100 °C, resulting in cross-linked materials such as hydrogels, shape memory materials, adhesives, or coatings [49]. These problems can be completely eliminated by catalyzed azide–alkyne cycloaddition introduced by Rolf Huisgen [50]. A 1,3-dipolar cycloaddition between an azide and a terminal or internal alkyne yields a 1,2,3-triazole which can be carried out at room temperature while in the presence of a copper catalyst (Scheme 13.4). This reaction, though capable of being completed with Cu (I) (e.g., CuBr, CuI), performs best when a mixture of Cu (II) (e.g., Cu_2SO_4) is utilized alongside a reducing agent (e.g., sodium ascorbate), thus producing Cu (I) in situ. Owing to the versatility of CuAAC's cross-linking ability, it can be applied as a powerful self-healing mechanism. Semi-encapsulation and encapsulation approaches are applicable for this purpose. A one-component healing mechanism is not possible by using this tool since a cross-linked mass would be the final product because CuAAC proceeds even in the absence of catalyst, albeit slowly:

(a) Semi-capsulation method for CuAAC
The main strategy employed by the semi-capsulation method is that a thermoplastic matrix is prepared with either azide or alkyne functionality with an embedded copper catalyst (preferably CuBr $(PPh_3)_3$) and microcapsules containing the complementary functionality. As soon as the damaging event occurs, the liquid cross-linker will dissolve the embedded catalyst from the matrix, initiating the cross-linking reaction between the azide and alkyne, thus healing the cracks.

(b) Capsulation methods for CuAAC
As previously mentioned, this method utilizes binary capsules. Some of the capsule contents are listed below. This healing method can be utilized for both thermoplastic and thermosetting plastics. A schematic representation of the method is shown in Scheme 13.5. Star-shaped or hyperbranched azides/alkynes containing reagents with sufficient room temperature fluidity are beneficial for this purpose (Fig. 13.5). Examples of some alkynes and azides are given below:


Multifunctional azides
Multifunctional alkynes
N3
HO
OR
low M.W.

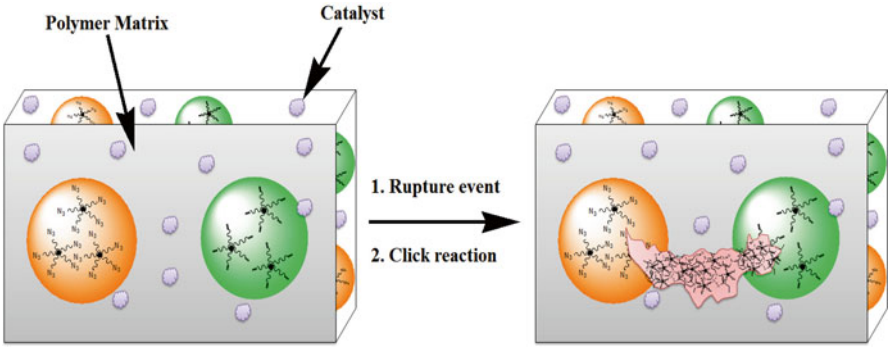
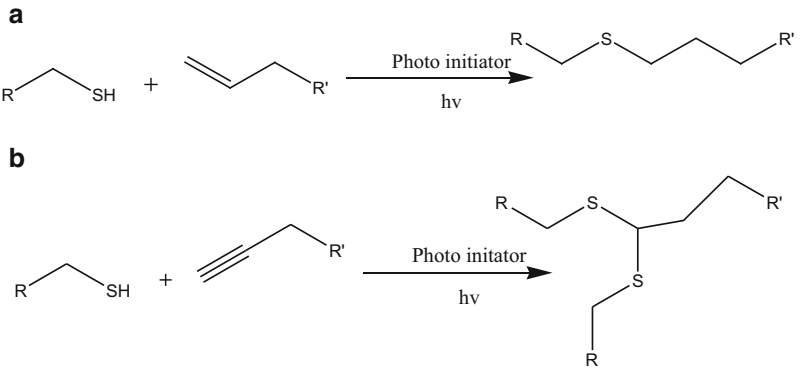


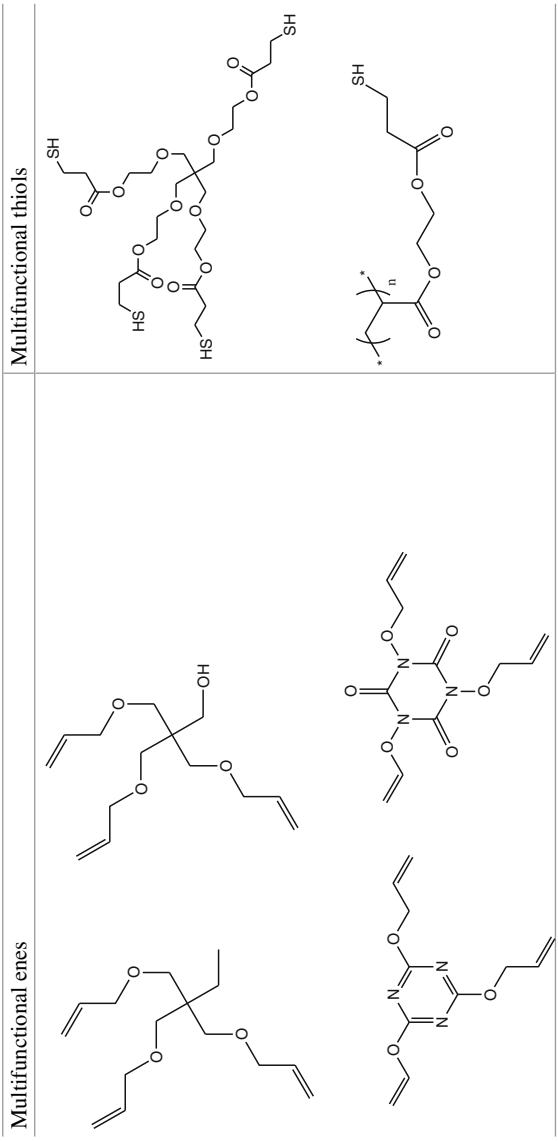
Fig. 13.5 Representation of CuAAC-based self-healing process via microcapsulation method [11]



Scheme 13.5 General mechanism of thiol–ene reaction (**a**) and thiol–yne reaction (**b**)

13.3.3 Thiol–ene/yne Click Reaction

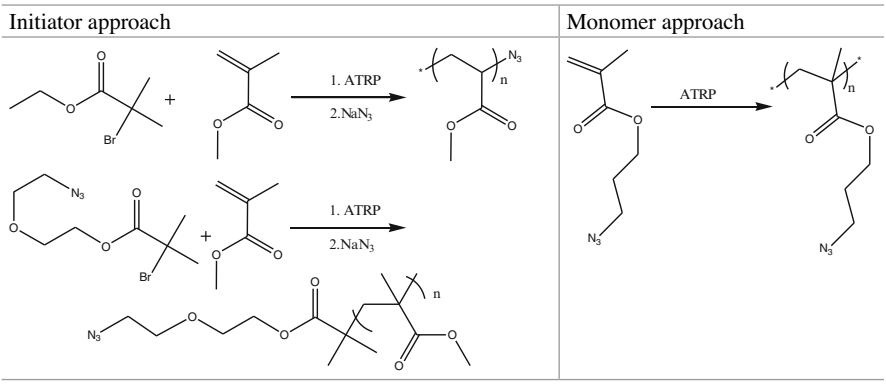
Even though the azide–alkyne cycloaddition reaction eliminates the requirement of high temperature, it lacks in the purity of material due to the presence of biotoxic copper salts. This problem can be overcome by photochemically triggering thiol–ene and thiol–yne click reactions (Scheme 13.5). Moreover, these click reactions attract the considerable attention of scientists due to their ability in combining all the advantages of click chemistry and the potential of light-triggered reactions, thus permitting a spatially and temporally controlled self-healing process. Although both of these click reactions are similar, thiol–yne polymerization reactions complement the more well-known thiol–ene polymerization processes, with the added advantage of increased functionality. The application of these two reactions in self-healing material synthesis is mechanistically similar to the azide–alkyne cycloaddition reaction mentioned above (i.e., semi-capsulation and capsulation methods). The only difference is that instead of a copper catalyst, it requires a photoinitiator (e.g., 2,2-dimethoxy-2-phenylacetophenone) to be embedded in the matrix. The major drawback in designing self-healing materials by these two methods is that the matrix must be transparent, which limits its applicability considerably. Examples of some typical multifunctional enes and thiols are given below:


Multifunctional thiols
Multifunctional enes

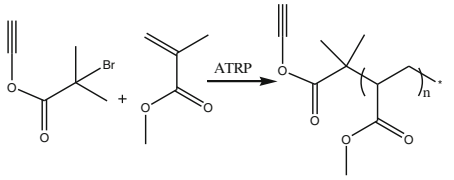
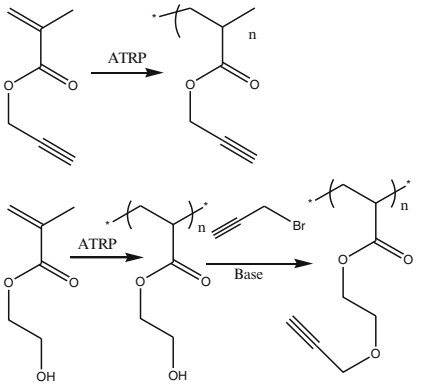
13.4 Combination of ATRP and Click Chemistry to Synthesize Self-Healing Material

As already mentioned, ATRP is the most versatile controlled radical polymerization technique available, while click chemistry is the most promising coupling technique currently known in the field of polymer chemistry. There are a range of possibilities where ATRP can be further broadened by the integration of click chemistry. A combination of these two techniques can provide numerous ways of designing self-healing polymers. Some of these methods are listed below. The monomers and initiators that are used are for representative purpose only. Multifunctional products can be obtained by using a corresponding multifunctional initiator.

13.4.1 ATRP Used for Synthesis of Azide End-Functionalized Polymers

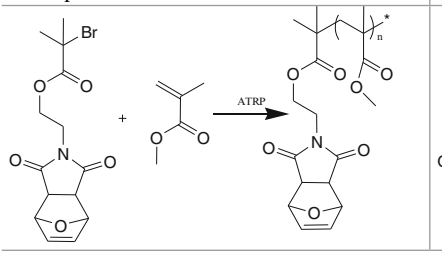
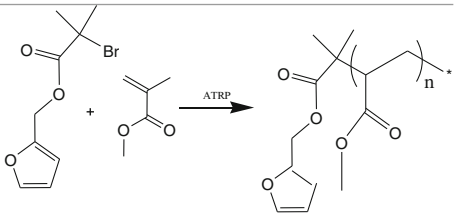


13.4.2 ATRP Used for Synthesis of Alkyne End-Functionalized Polymers

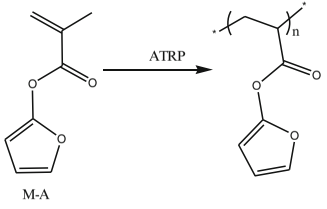
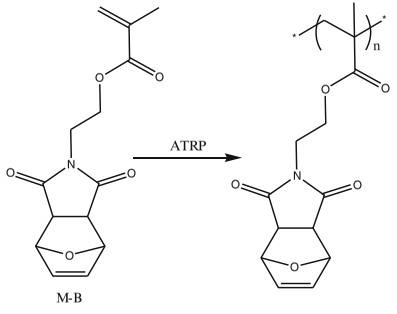
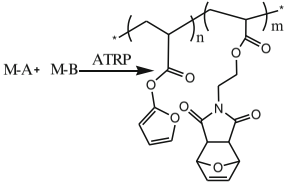
Initiator approach	Monomer and post-polymerization modification approach
	

13.4.3 ATRP Used for Synthesis of Diene-/Dienophile-Functionalized Polymers

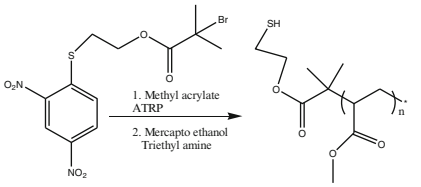
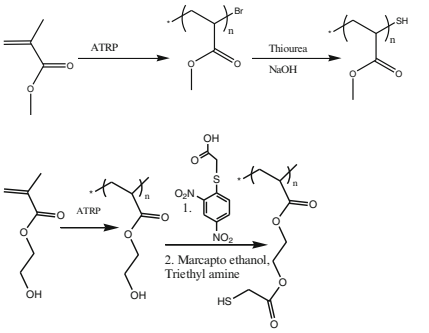
(a) Initiator approach

Dienophile	Diene
	

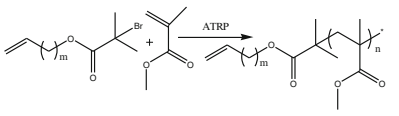
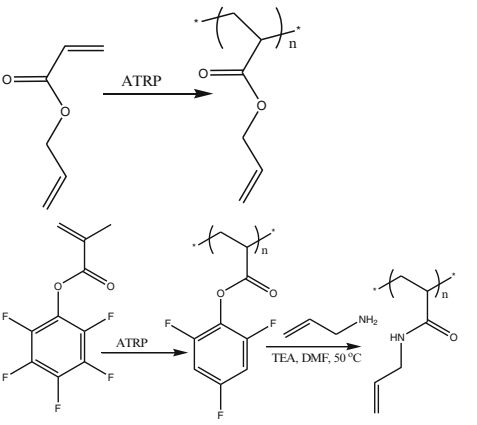
(b) Monomer approach

Diene-containing polymer	Dienophile-containing polymers	Both diene- and dienophile-containing polymer
		

13.4.4 ATRP Used for Synthesis of Thiol-Containing Polymers

Initiator approach	Post-polymerization modification
	

13.4.5 ATRP Used for Synthesis of Ene-Containing Polymers

Initiator approach	Monomer approach
	

13.5 Conclusion

To summarize, the combination of ATRP and click chemistry is an inexorable route for preparing highly efficient, easy-to-implement, and highly functional tailor-made polymers that chemists find highly desirable. This combination has been tremendously advanced since the introduction of the click chemistry concept by the cumulative efforts of a large number of research groups all over the world. These developments on the preparation of new well-defined clickable polymers by ATRP enabled straightforward access to a large variety of self-healing polymers and polymeric composites. This chapter demonstrated both individual and numerous combinations of ATRP and click chemistry to aid in the design of efficient intrinsic as well as extrinsic self-healing polymeric materials. Finally it can be concluded that the combination of ATRP and click chemistry methods will continue to thrive in the near future and in advancing the tailoring of new functional polymeric materials with more effective healing properties.

References

1. Chen X, Dam M, Ono A, Mal K, Shen A, Nutt H, Sheran SR, Wudl K (2002) Science 295:1698
2. Chen X, Wudl F, Mal A, Shen H, Nutt SR, Sheran K (2003) Macromolecules 36:1802
3. White SR, Sottos NR, Guebelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S (2001) Nature 409:794
4. Nathalie K, Guimard K, Kim O, Jiawen Z, Stefan H, Friedrich GS, Christopher BK (2012) Macromol Chem Phys 213:131
5. Brown EN, Sottos NR, White SR (2002) Exp Mech 42:372
6. Keller MW, White SR, Sottos NR (2007) Adv Funct Mater 17:2399
7. Guan Z, Roland JT, Bai JZ, Ma SX, McIntire TM, Nguyen M (2004) J Am Chem Soc 126:2058
8. Varley RJ, Zwaag VD (2008) Polym Test 27:11
9. Tadano K, Hirasawa E, Yamamoto H, Yano S (1989) Macromolecules 22:226
10. Zare P, Mahrova M, Tojo E, Stojanovic A, Binder WH (2013) J Polym Sci A Polym Chem 51:190
11. Gragert M, Schunack M, Binder WH (2011) Macromol Rapid Commun 32:419
12. Saiki BJ, Gogoi P, Sharmah S, Dolui SK (2015) Polym Int 64:437
13. Matyjaszewski K (2012) Macromolecules 45:4015
14. Quirk P, Kim J (1991) Rubber Chem Technol 64:450
15. Zhang L, Liu W, Lin L, Chen D, Stenzel MH (2008) Biomacromolecules 9:3321
16. Laurent BA, Grayson SM (2006) J Am Chem Soc 128:4238
17. Van Camp W, Germonpre V, Mespouille L, Dubois P, Goethals EJ, Du Prez FE (2007) React Funct Polym 67:1168
18. Durmaz H, Karatas F, Tunca U, Hizal G (2006) J Polym Sci A Polym Chem 44:3947
19. Mantovani G, Lecolley F, Tao L, Haddleton DM, Clerx J, Cornelissen JJLM, Velonia K (2005) J Am Chem Soc 127:2966
20. Gao H, Matyjaszewski K (2006) Macromolecules 39:4960
21. White SR, Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR (2011) Am Sci 99:392
22. Murphy EB, Wudl F (2010) Prog Polym Sci 35:223

23. Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR (2010) Annu Rev Mater Res 40:179
24. Zhang MQ, Rong MZ (2012) Sci China Chem 55:648
25. Müller M, Dardin A, Seidel U, Balsamo V, Iván B, Spiess HW, Stadler R (1996) Macromolecules 29:2577
26. Greenland BW, Burattini S, Hayes W, Colquhoun HM (2008) Tetrahedron Lett 64:8346
27. Kalista SJ, Ward TC, Oyetunji Z (2007) Mech Adv Mater Struct 14:391
28. Chen Y, Kushner AM, Williams GA, Guan Z (2012) Nat Chem 4:467
29. Rahman MdA, Penco M, Spagnoli G, Peroni I, Ramorino G (2012) AIP Conf Proc 163:1459
30. Hart LR, Nguyen NA, Harries JL, Mackay ME, Colquhoun HM, Hayes W. doi:10.1016/j.polymer.2015.03.028
31. Hohlbein N, Pelzer T, Nothacker J, von Tapavicza M, Nellesen A, Datta H, Schmidt AM (2013) 'Self-healing processes in ionomeric elastomers', ICSHM, 680.
32. Tasdelen MA (2011) Polym Chem 2:2133
33. Kötteritzsch J, Hager MD, Schubert US (2013) One-component intrinsic self-healing polymer for coatings based on reversible crosslinking by Diels-Alder-cycloadditions, ICSHM, 624
34. Yang J, Keller MW, Moore JS, White SR, Sottos NR (2008) Macromolecules 41:9650
35. Ghosh D, Sharman R, Rao HR, Upadhyaya S (2007) Decis Support Syst 42:2164
36. Kessler MR, Sottos NR, White SR (2003) Compos A 34:743
37. Hayes SA, Jones FR, Marshiya K, Zhang W (2007) Compos A 38:1116
38. Kirkby EL, Michaud VJ, Månson JAE, Sottos NR, White SR (2009) Polymer 50:5533
39. Noh HH et al (2013) Express Polym Lett 7:88
40. Hua J, Chenb HQ, Zhanga Z (2009) Mater Chem Phys 118:63
41. Halasa AF (1981) Rubber Chem Technol 54:627
42. Kolb HC, Finn MG, Sharpless KB (2001) Angew Chem Int Ed 40:2004
43. Rostovtsev VV, Green LG, Fokin VV, Sharpless KB (2002) Angew Chem Int Ed 41:2596
44. Tornoe CW, Christensen C, Meldal M (2002) J Org Chem 67:3057
45. Kumaraswamy G, Ankamma K, Pitchaiah A (2007) J Org Chem 72:9822
46. Schunack M, Gragert M, Döhler D, Michael P, Binder WH (2012) Macromol Chem Phys 213:205
47. Evans RA (2007) Aust J Chem 60:384
48. Weizman H, Nielsen C, Weizman OS, Nasser SN (2011) J Chem Educ 88:1137
49. Döhler D, Michael P, Wolfgang HB (2012) Macromolecules 45:3335
50. Huisgen R (1961) Proc Chem Soc 357