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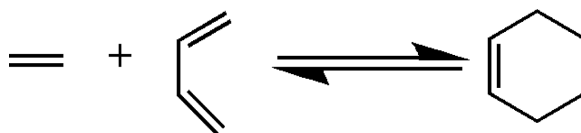
## Reversible Diels–Alder Cycloaddition for the Design of Multifunctional Network Polymers

*Amy M. Peterson and Giuseppe R. Palmese*

### 9.1 Introduction

Click chemistries such as the Diels–Alder reaction have been used to prepare many novel and difficult to achieve multifunctional polymer networks.<sup>1–9</sup> Such chemistries are popular because they offer high yields and minimal side reactions under mild reaction conditions. The Diels–Alder reaction is a cycloaddition of a diene and a dienophile to form a substituted cyclohexene.<sup>10–12</sup> In some cases, the reaction is thermally reversible. This reversibility makes the Diels–Alder reaction particularly desirable for the development of multifunctional polymer networks.<sup>13</sup>

The Diels–Alder reaction, shown in its general form in Figure 9.1, was discovered by Otto Diels and Kurt Alder in the 1920s. A substituted cyclohexene is formed in this reaction through the [4 + 2] cycloaddition of a diene and a dienophile. This reaction proceeds through unsymmetrical transition states.<sup>14</sup> While the simplest dienophile, ethylene, reacts poorly with dienes, there are many dienes and dienophiles that undergo the Diels–Alder cycloaddition readily. Conjugated dienes react as long as they can achieve a *cisoid* geometry and cyclic dienes tend to be more reactive than open chain dienes.<sup>11</sup> The Diels–Alder reaction is reversible when the reactants are stable molecules or when one can be consumed in a side reaction. The reverse reaction is known as the retro-Diels–Alder reaction. The chemical structures of well-known dienes, dienophiles and adducts as well as the


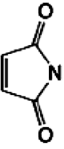
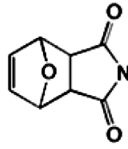
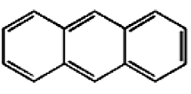
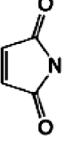
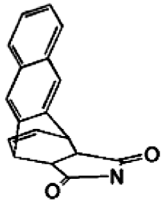

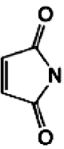
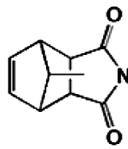


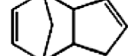


**Figure 9.1** Generalized Diels–Alder reaction of a dienophile with a diene.

temperatures at which they undergo the forward and reverse Diels–Alder reactions are shown in Table 9.1.

Much of the literature has focused on the reaction of furan (diene) and maleimide (dienophile), presumably because of the mild conditions under which the retro Diels–Alder reaction occurs.<sup>15–54</sup> However, the reactions of maleimide with cyclopentadienone,<sup>55</sup> fulvene,<sup>56</sup> pyrone,<sup>57,58</sup> and anthracene,<sup>4–6,49,59–62</sup> of benzene with cyclopentadienone<sup>63–65</sup> and of quinone with cyclopentadiene<sup>66–69</sup> have been investigated as well. Cyclopentadiene has also been shown to react reversibly with itself via the Diels–Alder reaction, acting as both the diene and the dienophile.<sup>70–80</sup> Additionally, poly(vinyl chloride) demonstrates reversible crosslinking when thermal degradation results in the formation of polyenes in the polymer chain.<sup>81–84</sup>

**Table 9.1** Some well known thermoreversible Diels–Alder reactions

Diene	Dienophile	Adduct	Forward reaction upper limit - reverse reaction lower limit	References
Furan 	Maleimide 		60-90 °C	17, 34, 37, 39, 40, 47, 48
Anthracene 	Maleimide 		250-300 °C	60
Fulvene 	Maleimide 		30-100 °C	56
Cyclopentadiene 	Cyclopentadiene 		80-180 °C	8, 72, 78, 79

Since the discovery of the Diels–Alder reaction over 80 years ago, many groups have investigated important aspects of this reaction's behavior such as reaction mechanisms, as well as thermodynamic and kinetic concerns. As a whole these inquiries have elucidated factors that influence reactivity and reversibility, including the chemical nature of the diene–dienophile selected, steric considerations, reaction conditions, solvents and diffusion limitations. The following is not meant to be a comprehensive summary of these works but rather one that highlights important aspects that need to be considered when polymer networks containing Diels–Alder function linkages are designed.

The Diels–Alder adduct exhibits *endo* and *exo* isomers with different properties. The major product of the Diels–Alder reaction is typically the *endo* adduct. This preference has been explained with secondary orbital interactions, inductive or charge-transfer interactions and overlap of  $\pi$  orbitals.<sup>11</sup> Solvent choice for the reaction of furan and maleimide in solution does not affect the isomer produced, although reaction temperature does. At 90 °C, the *exo* product, with a melting temperature of 162 °C, is achieved. Performing the reaction at 25 °C produces the *endo* isomer, with a melting temperature of 131 °C.<sup>85</sup> Herndon *et al.* discovered that *exo*-dicyclopentadiene is less reactive than the *endo* isomer by an order of magnitude.<sup>71</sup>

Neukam and Grimme found that the retro-Diels–Alder reaction was exothermic if it combined the formation of an aromatic group with the release of ring strain from the adduct.<sup>84</sup> They also showed that the cycloreversion of the cyclopentadiene and 5-cyanocyclopentadiene adduct can be accelerated by deprotonation. Loss of basicity was also proposed to significantly increase the rate of cycloreversion.<sup>86</sup> Additionally, Brand and Klapper found that substituted furans undergo Diels–Alder reaction with normal electron demand and that the reactivity of forward and reverse reactions can be controlled by changing the donor/acceptor character of the substituent.<sup>87</sup>

The first mention of Diels–Alder reaction order was made by Kwart and King.<sup>27</sup> They reported that the forward reaction of a diene and a dienophile generally followed second-order kinetics. This finding was later corroborated,<sup>44,51,52,66,67</sup> although pseudo-first-order conditions can be approximated with an excess of either diene or dienophile.<sup>9,69,88,89</sup> Liu and Hsieh found the activation energy of the forward Diels–Alder reaction between furan and maleimide groups to be 67 kJ mol<sup>-1</sup> in one case<sup>51</sup> and 32.1 kJ mol<sup>-1</sup> in another.<sup>52</sup> In other studies the reverse reaction was found to follow a first-order rate law with an activation energy of 21 kJ mol<sup>-1</sup>.<sup>42</sup> There have been numerous investigations of the forward and reverse reaction rates and it is thought that for each system an equilibrium is established over a range of temperatures so that the equilibrium concentration of Diels–Alder linkages can be controlled by setting a temperature in this range. However, comprehensive experimental studies have not been conducted to establish the quantitative relationship between temperature and equilibrium composition in polymer systems.

The influence of surfaces on the Diels–Alder reaction has also been studied. In the case of quinone immobilized on a gold surface reacting with cyclopentadiene, the reaction was found to follow a pseudo-first-order rate law, but the rate constant is not linearly related to diene concentration.<sup>69</sup> Gawalt and Mrksich propose that this behavior is the result of electrochemical oxidation, which creates two forms of quinone, with one that is two orders of magnitude more reactive than the other. Production of the highly reactive form is the rate-determining step in this reaction. Kwon and Mrksich studied the effect of steric hindrance on reaction rate for the reaction of cyclopentadiene with benzoquinone contained within a self-assembled monolayer (SAM).<sup>68</sup> The rate constant decreased significantly when the quinone was positioned below the monolayer interface. When the quinone was positioned

above the other groups of the SAM, a rate constant between 0.18 and 0.22  $\text{M}^{-1} \text{s}^{-1}$  was found, while the rate for quinone below the monolayer interface was approximately 0.03  $\text{M}^{-1} \text{s}^{-1}$ .

Although click chemistries are often selected because of the dearth of side reactions, there are a few secondary reactions in which typical Diels–Alder dienes and dienophiles participate. Maleimides react readily with amines, alcohols and thiols through Michael addition.<sup>46,91</sup> Maleimides can also homopolymerize.<sup>92</sup> Furfuryl groups have been found to be unstable and can ring open or form dihydro- or tetrahydrofuran rings.<sup>13,80</sup> The Diels–Alder adduct may degrade via aromatization to form an irreversible linkage.<sup>13,29</sup> Vinyl addition of some dienes and dienophiles has been shown.<sup>76</sup> Additionally, steric hindrance of reactants can affect the extent of the Diels–Alder reaction.<sup>15</sup> Some researchers have applied these side reactions in the preparation of novel polymer networks.<sup>46,91,92</sup> The focus of this chapter is the application of reversible Diels–Alder chemistries to polymer networks to provide additional functionality. Polymer network design considerations are presented first, followed by examples of polymer networks with Diels–Alder linkages providing additional functionality are presented. We begin the discussion of Diels–Alder functional systems with linear polymers, which, although not network polymers, have been investigated thoroughly and can provide important information about the behavior of the Diels–Alder reaction in a polymer system. A number of reversibly crosslinked systems are discussed including remoldable crosslinked materials, thermally removable encapsulants, reversibly crosslinked polymer-solvent gels, remendable materials, recyclable thermosets, and smart materials.

## 9.2 Design of Polymer Networks

A polymer network is defined as a polymeric system in which the mer units are connected such that numerous paths exist through the macromolecule.<sup>93</sup> Crosslinked networks are desirable because of their mechanical properties, thermal stability and insolubility in solvents. Once crosslinked, a polymer network cannot melt. This chapter focuses on polymer networks given additional functionality with the incorporation of reversible Diels–Alder linkages because of the ubiquity of crosslinked systems and because of the novel characteristics of polymer networks containing such bonds. In our discussion of networks, we will also consider branched systems such as dendrimers.

When crosslinks are formed with Diels–Alder bonds, the resulting material is a crosslinked material at ambient conditions but can be remolded and remended at increased temperatures.<sup>16,23,94–96</sup> One interesting result of incorporating thermoreversible linkages is that chains within the system can diffuse and stress can relax, allowing for creep of the crosslinked network.<sup>97</sup>

In the design of networks containing reversible linkages, the concentration, placement and type of reversible bonds are very important considerations. One method for making such crosslinked networks using diene and dienophile reactive groups is to form polymer chains with pendant functional groups (diene or dienophile) that crosslink via reaction with difunctional molecules<sup>16,28,77</sup> or other polymer chains<sup>72,73,78,79</sup> with the complementary functionality (dienophile or diene). The other method relies on the reaction of multifunctional ( $f \geq 3$ ) monomers to form a network.<sup>70</sup> If the first method is used, gelation generally occurs at significantly lower conversion than the second method because the polymer chains

have more functional groups than monomers. The statistical approaches of Flory<sup>98,99</sup> and Stockmayer<sup>100,101</sup> state that, as the number of functional groups increases, the percolation conversion decreases according to the following equation:

$$p_c = \frac{1}{(f - 1)^{1/2}} \quad (9.1)$$

Equation (9.1) assumes a stoichiometric mixture of dienes and dienophiles with a difunctional unit consisting of one type of functional group (A) and a branching unit consisting of the other type of functional group (B). Additionally, equal reactivity of A and B, reactivity independent of conversion, and no intramolecular reaction prior to gelation are assumed. Based on Equation (9.1), gelation of a system with branching units of  $f = 4$  (such as those of Chen *et al.*<sup>21–23</sup>) is predicted to occur at  $p_c = 0.577$ . However, the critical conversion of a furan-modified polystyrene,  $f = 94.2$  (Goussé *et al.*<sup>18</sup>), reacting with a bismaleimide, is 0.104.

As shown in Table 9.1, the choice of diene and dienophile affects the temperature at which the Diels–Alder adduct forms and breaks or forms and degrades. Desired properties and applications dictate the use of various Diels–Alder reactants. Additionally, and as mentioned in the previous section, equilibrium composition is influenced by temperature over a considerable range, so mechanical behavior would be influenced not only by typical molecular mobility effects but also by changes in polymer structure like crosslink density. An example of these new factors that must be considered in the design of polymer networks using reversible linkages is the influence of the retro-Diels–Alder reaction on viscoelastic behavior. The time-temperature superposition principle states that time is equivalent to temperature for viscoelastic materials like polymers. A phenomenon that occurs over a long time scale at a low temperature is equivalent to the phenomenon that occurs over a short time scale at a high temperature. As a result, behavior can be determined at a wider range of temperature and frequencies than can be measured. One way to relate time and temperature is through the Williams–Landel–Ferry (WLF) equation, which is given below.<sup>90,102</sup>

$$\log_{10} a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (9.2)$$

In the WLF equation,  $a_T$  is the shift factor and is positive if the curve is to the left of the reference and is negative if the curve is to the right of the reference.  $T$  is the measured temperature and  $T_0$  is the reference temperature, while  $C_1$  and  $C_2$  are constants. In many cases,  $C_1 = 17.4$  and  $C_2 = 51.6$ . Gotsmann *et al.* found that the indentation kinetics of a polymer comprised of a trisfuran and bismaleimide deviate from the WLF equation.<sup>50</sup> Deviation from WLF behavior is expected in polymers containing Diels–Alder linkages because the number of bonds, and therefore the inherent viscoelastic behavior of the material, is temperature dependant.

### 9.3 Application of Diels–Alder Linkages to Polymer Systems

Diels–Alder bonds have been applied to many types of networks to form materials designed for a variety of uses, ranging from biomedical and encapsulant<sup>24–26,39</sup> technologies to recyclable<sup>19,53</sup> and remendable materials.<sup>94,95</sup> The following sections are organized

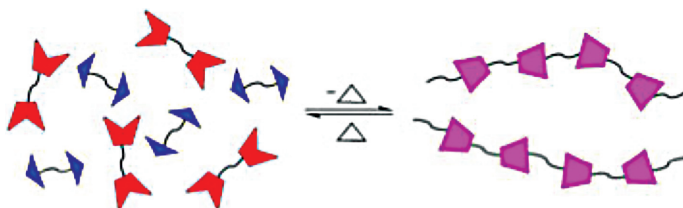
according to the type of polymer developed and potential applications. Taken as a whole they provide a comprehensive review of polymer architectures that can be created to provide multifunctionality based on the thermoreversible nature of the Diels–Alder linkage.

### 9.3.1 Molecular Weight Control of Linear Polymers

Although linear polymers are not considered to be polymer networks, a significant portion of the literature on reversible Diels–Alder linkages is concerned with noncrosslinked systems.<sup>12</sup> Additionally, much of the early work in Diels–Alder-based polymers was concerned with linear polymers.<sup>55,56,70,76,104,105</sup> Diels–Alder bonds are desirable in linear polymers for control of chain length,<sup>74</sup> control of processing viscosity<sup>87</sup> and for improved recyclability.<sup>105</sup> Ladder polymers have also been prepared using Diels–Alder bonds.<sup>106</sup>

The first mention of Diels–Alder polymers appears in the patent literature. Upon prepared copolymers of *p*-xylene bis(5-cyclopentadiene) and cyclopentadiene.<sup>70</sup> Cure conditions dictated the physical properties of the resulting polymer. Fusible polymers were obtained with low temperature cure short, high-temperature cure cycles. Insoluble polymers were probably formed as a result of vinyl addition.<sup>76</sup> Kraiman prepared permanently bonded linear polymers via the reaction of bismaleimide with cyclopentadienone<sup>55</sup> and alpha pyrone.<sup>55</sup> In both cases, polymerization proceeded through the Diels–Alder reaction, the product of which condensed a smaller group (carbon monoxide and carbon dioxide, respectively) and then homopolymerized. Similar polymers include the copolymer of bismaleimide and thiophene dioxide, which emitted sulfur dioxide,<sup>103</sup> the copolymer of bismaleimide and cyclopentadienone, which emitted carbon monoxide,<sup>104</sup> and the linear polymer of bismaleimide and bispyrone, which emitted carbon dioxide.<sup>57</sup>

Figure 9.2 is a schematic showing the thermally reversible behavior of a linear polymer based on Diels–Alder linkages. The first example of reversibly bonded polymers appears in work from Stille and Plummer.<sup>76</sup> Since cyclopentadiene can act as a diene and a dienophile, dicyclopentadiene was homopolymerized and also copolymerized with *p*-benzoquinone and a bismaleimide. At increased reflux temperatures, inherent viscosity decreased, indicating the occurrence of the retro-Diels–Alder reaction. Another copolymer formed from the reaction of cyclopentadiene with maleimide shows chain extension at 80 °C.<sup>74</sup> Reaction equilibrium was shifted towards the reactants at higher temperature, while lower temperatures decreased the reaction rate. However, even when polymerized at 80 °C these opposing phenomena prevented the formation of high-molecular-weight polymers.



**Figure 9.2** Schematic of a reversibly forming linear polymer of a bisdiene and a bisdienophile. Dienes are shown as notched trapezoids, dienophiles are shown as triangles and Diels–Alder adducts are shown as trapezoids.

A similar effect was shown in the polymerization of bisfuran with bismaleimide. Kuramoto *et al.* observed that, as the reaction temperature increased from 25 to 60 °C, reaction rate increased, but chain length decreased.<sup>34</sup> Additionally, spectroscopic analysis showed that after heating the polymerized system at 90 °C for 2 h, only 20% of the initial maleimide was recovered. This suggests that either some of the Diels–Alder adducts could not be reversed at this temperature as a result of the chemical equilibrium or that secondary maleimide reactions occurred. Teramoto *et al.* reported maximum molecular weights for polymerization temperatures of 70 and 55 °C for two bismaleimides.<sup>53</sup> Molecular weight was shown to decrease for reaction temperatures above 90 °C and gel permeation chromatography demonstrated that the retro-Diels–Alder reaction proceeded rapidly above 100 °C. A copolymer of bismaleimide and bisfulvene also displayed reversibility of Diels–Alder adducts.<sup>56</sup> When heated above 60 °C the polymer demonstrated bond reversal through changes in viscosity. Temperature-controlled viscosity and molecular weight were achieved for linear polymer systems by Brand and Klapper.<sup>87</sup> Polymerization of bisanthracene and bismaleimide was reported by Grigoras and Colotin.<sup>60</sup> The product was an oligomer, perhaps due to steric effects or equilibrium with the retro-Diels–Alder reaction at the cure temperature of 120 °C. However, thermogravimetric analysis indicates that the retro-Diels–Alder reaction occurs between 250 and 300 °C in these systems.

Siloxane-modified bisfurans have been prepared and polymerized with bismaleimides for application in electronics or coatings.<sup>29</sup> To improve thermal stability of the material, the Diels–Alder adduct was aromatized by refluxing the solid product in acetic anhydride for 2 h. Aromatization of the Diels–Alder adduct was also used to prepare thermally stable polyimides<sup>31</sup> and linear polymers bearing pendant cyano groups<sup>107</sup> that could be further stabilized by crosslinking through said cyano groups.

Ladder polymers have been synthesized via Diels–Alder reaction. Blatter and Schlueter formed a soluble ladder polymer from a bisdiene and a bisdienophile.<sup>108,109</sup> No mention was made as to the reversible nature of this material. Kintzel *et al.* also prepared a ladder polymer system.<sup>106</sup>

Monomers containing both diene and dienophile functionality are of interest because a 1:1 stoichiometric ratio is always achieved. Mikroyannidis prepared AB monomers from furfuryl-substitution of maleimic acids<sup>31–33</sup> Goussé and Gandini questioned the success of Mikroyannidis based on limited polymer characterization and prepared 2-furfurylmaleimide themselves.<sup>35</sup> The polymerization product following reaction at 90–180 °C for 15 min to several hours was a brown solid insoluble in most solvents. No mention of reversibility was made by either group; however, cure temperatures may have degraded the maleimide<sup>17</sup> or caused vinyl addition polymerization.<sup>76</sup> Crosslinking through a secondary reaction is apparent in the product achieved by Goussé and Gandini due to its insolubility.

Grafting is also possible using the Diels–Alder reaction. Jones *et al.*<sup>59</sup> and Vargas *et al.*<sup>61</sup> reported poly(ethylene terephthalate) (PET) with anthracene groups. Reaction of these anthracenes with substituted maleimides provided hydrophobic and hydrophilic materials, depending on the type of maleimide used. This process can be applied to thin films since the Diels–Alder reaction occurs below the melting temperature of the polymer.

Compounds with potential biological applications have been prepared through diene modification of poly(ethylene glycol) (PEG) derivatives and subsequent reaction with maleimides.<sup>111,112</sup> Substitution of the maleimide can provide novel PEG derivatives. Block

copolymers were developed based on maleimide- and anthracene functionalization of PEG, poly(methyl methacrylate) (PMMA), polystyrene (PS) and poly(*tert* butyl acrylate) (PtBA).<sup>4</sup> Controlled synthesis was achieved by protecting maleimide groups with furan. When block copolymer synthesis was desired, the system was heated to 110 °C, cleaving the furan and allowing for reaction between maleimide and anthracene terminated blocks. A similar strategy was also used by Durmaz *et al.* to graft PEG onto PS chains.<sup>49</sup>

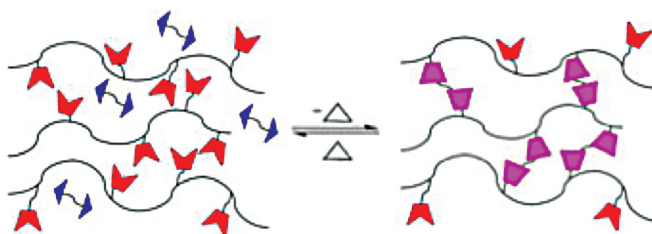
### 9.3.2 Remoldable Crosslinked Materials

Thermosets are desirable for many applications because of their mechanical properties, thermal stability, and resistance to solvents. However, once cast, crosslinked systems cannot be reformed. The desire to create remoldable crosslinked networks was the catalyst for developing polymers with thermoreversible crosslinks. One way to do this is shown schematically in Figure 9.3, in which linear polymers with pendant dienes/dienophiles crosslink through reaction with bisdienes/bisdienophiles.

Craven was the first to report on a reversibly crosslinking network with chains bearing furans crosslinked via reaction with bismaleimides. Upon heating to 120–140 °C the material was capable of being reshaped. Although high reversal temperatures were used, Craven warns, “‘Reversed’ does not mean that the crosslinked polymer product can be completely converted to its original components, but that it becomes a more plastic material, capable of being formed and shaped’.”<sup>16</sup> This observation may be the result of secondary crosslinking, perhaps through homopolymerization of maleimides or aromatization of Diels–Alder adducts.

In another example, anthracene-functionalized PET was found to reversibly crosslink in the presence of bismaleimides, even when the PET copolymer contained just 2 mol% of the anthracene unit.<sup>59</sup> Crosslinking was partially (27%, according to <sup>1</sup>H NMR) reversible upon heating to 250 °C for 7 h. Reversible Diels–Alder linkages have also been applied to elastomeric siloxane-based polymers, with the motivation of developing a recyclable material for tires. In this system, pendant furans react with bismaleimides at room temperature and adducts break apart at 80 °C.<sup>40</sup>

When cyclopentadiene, which can act as diene and dienophile, was used as the pendant functional group, linear polymers crosslinked via reaction with each other. Remolding



**Figure 9.3** Schematic of a reversibly crosslinking system comprised of a diene-functionalized linear polymer with a bisdienophile. Dienes are shown as notched trapezoids, dienophiles are shown as triangles and Diels–Alder adducts are shown as trapezoids.



was possible in one system when heated to 150–400 °C, although the preferred temperature range was 200–300 °C.<sup>77</sup> Kennedy and Castner also observed gelation of a cyclopentadienylated polymer. When heated to 215 °C, the system was insoluble in hexachlorobutadiene; however, when heated to 215 °C in the presence of maleic anhydride, the polymer was soluble, demonstrating that crosslinking occurred through pendant cyclopentadienes.<sup>72,73</sup> This material behaved as an elastomer and could be shaped by a mold when cured at 170 °C.<sup>78</sup> A cyclopentadienylated polyphosphazene demonstrated crosslinking at 80 °C and crosslink decoupling at 160 °C.<sup>79</sup> However, degradation associated with a loss of crosslink reversibility as well as a mass loss of 15–35% was observed when the polymer was heated to 320 °C.

### 9.3.3 Thermally Removable Encapsulants

Encapsulants are used in the electronics industry to protect components from the environment. Thermosets are often used for their high strength, durability and resistance to heat and chemical degradation. However, it is sometimes desirable for these encapsulants to be removed. As a result, thermally removable encapsulants have been designed using the Diels–Alder chemistry.<sup>39,54</sup> These materials are similar in many ways to remoldable materials, except that the complete removal of the encapsulant is necessary. Small *et al.* reported on a thermally removable encapsulant from at least one bismaleimide and at least one trisfuran or tetrafulfuran cured below 90 °C.<sup>39</sup> Such encapsulants could be easily removed by heating above 90 °C, preferably in a polar solvent.

Thermally removable epoxies and polyurethanes were developed by Loy *et al.*<sup>25,26</sup> The epoxy-based system was prepared by reacting bismaleimide with furfuryl glycidyl ether to form a diepoxy, which reacted further with a diamine. Below 90 °C, the polymer is a thermoset, but above 90 °C the reverse Diels–Alder reaction dominates and adducts break apart. Two methods were proposed for the synthesis of polyurethanes: hydroxyl-bearing furan reacted with bismaleimide to form a diol, which was cured with a diisocyanate; and isocyanate-bearing furan reacted with bismaleimide to form a diisocyanate, which was cured with a diol.

Brock *et al.* developed a ‘smart’ encapsulant fluid capable of flowing into a system, polymerizing upon thermal stimulus and being removed upon further thermal stimulus.<sup>54</sup> The original encapsulant fluid contained a multifuran with  $f \geq 3$  and a multimaleimide with  $f \geq 2$ . Either the furans or the maleimides were protected with maleimides or furans, respectively, to prevent polymerization before it is desired. Upon heating, reactive groups were unprotected and capable of reacting with other monomers. Gelation was observed at room temperature in 3–6 h. The crosslinked network could then be removed by heating above 120 °C.

### 9.3.4 Reversibly Crosslinked Polymer–Solvent Gels

Because of the high crystallinity of many bismaleimides, a number of polymer networks have been prepared in solution, resulting in polymer–solvent gels. Such gels could be used for biomedical applications<sup>30</sup> or as stimuli-responsive gels,<sup>52</sup> for example. Since the polymer networks are thermoreversible, gels become liquid upon heating and reform gels upon cooling. The first mention of swelled networks based on Diels–Alder chemistry in the

literature was a copolymer of polystyrene and *N*-chloromethylmaleimide crosslinked with a bisfuran and a dicyclopentadiene.<sup>28</sup> When crosslinked with the bisfuran at 80 °C, gelation occurred in 15 min, and with dicyclopentadiene at 270 °C, gelation was observed within 5 min.

Thermally reversible hydrogels were prepared by modifying poly(*N*-acetylenimine) with maleimide and furan.<sup>30</sup> Hydrogels were synthesized at room temperature in the dark in methanol. Swelling of these gels was controlled by the degree of substitution as well as the temperature.

Canary and Stevens compared a copolymer of polystyrene and *N*-chloromethylmaleimide crosslinked with difurfuryl adipate and a polymer containing both furan and maleimide groups.<sup>80</sup> Gels of both were prepared with acetophenone as the solvent. The gel crosslinked with difurfuryl adipate became liquid after 2.5 min at 150 °C, while the gel crosslinked with the polymer liquefied in 15 s under the same conditions. However, these polymers, particularly the furan-modified one, are rather unstable and the authors question the practicality of using furfuryl-based polymer networks.

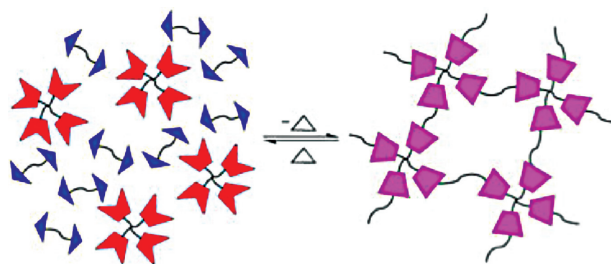
A copolymer of styrene and furfuryl methacrylate was crosslinked using a bismaleimide. Gelation was observed after 12 days in toluene for a 12 wt% solution of copolymer<sup>112</sup> and after 100 h in chloroform for a 25 wt% solution of copolymer.<sup>42</sup> Solutions in toluene could be reverted to liquid form after 1 h at 110 °C. Further studies showed that unconsumed bismaleimide remains at the gel point.<sup>44</sup> Additionally, the highest crosslinking efficiency was observed when the ratio of maleimide to furan was 0.5.<sup>45</sup>

Reversibly crosslinking polyamide gels of maleimide-bearing polyamides and trisfurans were prepared in *N,N*-dimethylacetamide and evaluated for their thermally-responsive nature.<sup>52</sup> As the maleimide content of the polymer increased, the time necessary to liquefy the gel increased. By drying gels at room temperature under vacuum, reversibly crosslinked polyamides were obtained.

Hybrid organic–inorganic gels have also been prepared. In one case Diels–Alder linkages were applied to couple the organic polymer and the silica matrix.<sup>43</sup> Homogeneity of the gel was controlled by reaction temperature. The linear polymer, a furan-bearing polystyrene, could be extracted from the gel by heating to 130 °C. Another hybrid gel consisted of an interpenetrating network (IPN) of furan- and maleimide-functionalized poly(2-methyl-2-oxazoline) and silica gel.<sup>37</sup> The IPN increases modulus and solvent resistance. Reaction efficiency, the fraction of reactive sites used, was 47%.

### 9.3.5 Remendable Materials

More recent work in reversibly bonded networks has focused on their application for thermally remendable materials. The first report of a thermally remendable polymer based on the Diels–Alder reaction came from Chen *et al.*<sup>21</sup> The polymer consisted of a tetrauran and a trismaleimide. Based on solid-state<sup>13</sup>C NMR, the bonds in this material were irreversible below 120 °C, showed 12% reversibility at 130 °C and showed 25% reversibility at 150 °C. Healing efficiency was evaluated by breaking a compact tension specimen, realigning the surfaces, heating at 120–150 °C for 2 h to break Diels–Alder bonds, cooling to room temperature to reform bonds across the crack surface, and retesting the specimen. Heating at 150 °C resulted in approximately 50% healing efficiency, while heating at 120 °C gave 41% healing efficiency. Although Chen *et al.* assert that the Diels–Alder reaction of furans



**Figure 9.4** Self-healing thermoset of a tetradiene and a bisdienophile. Dienes are shown as notched trapezoids, dienophiles are shown as triangles and Diels–Alder adducts are shown as trapezoids.

and maleimides is irreversible below 120 °C, work from our group and others shows that the reaction equilibrium strongly favors the reverse reaction at temperatures above 90 °C.<sup>113</sup> Differences in healing efficiencies for healing temperatures above 90 °C are more likely a result of higher reactant mobility associated with higher temperatures.

Chen *et al.* also prepared remendable networks using two bismaleimides, 1,8-bis(maleimido)-3,6-dioxaoctane (2ME) and 1,8-bis(maleimido)-1-ethylpropane (2MEP) and a tetrafulan.<sup>22</sup> A schematic representation of such a system is shown in Figure 9.4. These polymers are hard, colorless and transparent at room temperature. Unlike their previous system, which was synthesized in a solvent that was evaporated off during cure, the new materials were synthesized in bulk, thanks to lower melting point bismaleimides. The polymer network synthesized with 2ME could be remolded at 160 °C; however, healing efficiency could not be evaluated because the material changed shape at the healing temperature. The polymer network prepared with 2MEP softened at 180 °C. When healed at 115 °C for 30 min, the material exhibited 80% healing efficiency for the first heal and 71% healing efficiency for the second heal.

Plaisted and Nemat-Nasser also investigated the mechanical and healing properties of the 2MEP4F system from Chen *et al.*<sup>114</sup> They found a fracture toughness of 0.71 MPa m<sup>1/2</sup>. Interestingly, they discovered that healing at 85 °C for 30 min under reasonable pressure followed by 30 min at 95 °C was sufficient for obtaining maximum healing. This research relied on a different geometry for mechanical testing, the double cleavage drilled compression specimen, which had the distinct advantage of a self-arresting crack so that fractured samples were in one piece following testing. The geometry significantly eased the realignment of opposing crack surfaces. The healing efficiencies reported for 4MEP4F were generally above 98%, significantly higher than that reported by Chen *et al.* for the same material.

Additional work by Wudl and Chen focused on remendable polymers based on a variety of multifurans and multimaleimides with  $f \geq 3$ . As with their other systems, these materials are hard and transparent. Above 120 °C, approximately 30% of the Diels–Alder adducts reverted to furans and maleimides, which reformed Diels–Alder adducts when cooled.<sup>23</sup> Although no mention was made of secondary reactions such as adduct aromatization or maleimide homopolymerization, it seems likely that such phenomena were at work in this

system, since only 30% of the adducts broke apart at 120 °C, 30 °C above the temperature at which all adducts should have reverted to furans and maleimides.

One disadvantage of remendable materials using thermoreversible bonds, such as Diels–Alder adducts, is that the materials are not self-healing, that is, an external force is necessary to cause healing. This lack of autonomy is why these materials are characterized as remendable instead of self-healing.<sup>115</sup> In order to impart remendable materials with the ability to self-heal, arrays of conductive elements such as copper wires and coils were incorporated in fiber-reinforced composites of a trismaleimide tetrauran polymer from the Wudl group.<sup>116</sup>

Liu and Hsieh prepared two thermosetting systems that exhibited healing. The first polymer consisted of epoxy-based trisfurans and trismaleimides that were mixed in acetone and cured at 50 °C for 12 h. The retro-Diels–Alder reaction of the material was observed after heating at 170 °C for 30 min. However, a cut in the material healed following 2 h at 120 °C and 12 h at 50 °C.<sup>51</sup> Polyamides with maleimide and furan functionality were also crosslinked. A cut in the surface of the material was healed after 3 h at 120 °C and 5 days at 50 °C.<sup>20</sup> The low temperature healing is curious since the reverse reaction does not occur below 60 °C. However, healing is possible at 50 °C, provided there is sufficient energy to bring furans and maleimides in contact with each other across the cut surface, because the reversible nature of the Diels–Alder reaction means that bonds are continually being formed and broken to keep the reaction at equilibrium.

Atom transfer radical polymerization was used to synthesize polymethacrylates with pendant furans and known molecular weights, which were then crosslinked with bis-maleimide.<sup>117</sup> The Diels–Alder bonds were shown to be thermally mendable and fully reversible using Fourier Transform Infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC).

The most recent work in the area of remendable polymers based on the Diels–Alder reaction used dicyclopentadiene-based monomer. Upon heating of the monomer to 120 °C, the dicyclopentadiene opened via retro-Diels–Alder reaction, allowing the monomer to react with other cyclopentadienes. This formed a polymer backbone. Crosslinking of the system occurred through further reaction of backbone dicyclopentadiene with cyclopentadiene. The maximum healing efficiency achieved was 46%.<sup>75</sup>

### 9.3.6 Recyclable Thermosets

One disadvantage inherent in thermosetting polymers is the inability to reuse them. Once a thermoset has cured, it cannot be made to flow or mold to a different shape. However, if crosslinks are formed through reversible bonds, in theory the crosslinks can be removed generating a flowable material that can be recycled. Recyclable thermosets employing a number of reactions, including the Diels–Alder reaction of furan and maleimide, were proposed by Nakano *et al.*<sup>118</sup> Higher molecular weight monomer units were used because one condition of the material was that the properties of the base polymer not be compromised by recyclability. The polymer can be recycled by heating and filtering the system or by extracting monomer with solvent. Numerous other systems have been studied and are described below.

A random copolymer of styrene and furan-functionalized styrene was prepared and crosslinked with bismaleimide. Its recyclability was evaluated by heating at 130 °C in a

solution of 2-methylfuran. 2-Methylfuran acted as a trap, capturing the bismaleimide and preventing re-crosslinking.<sup>18</sup>

Watanabe and Yoshie developed recyclable polymers from furan-terminated poly(ethylene adipate) and bis- and tris-maleimides.<sup>19</sup> The copolymer of furan-terminated poly(ethylene adipate) and bismaleimide was a linear polymer, while the copolymer containing trismaleimide was a crosslinked network. Heating of both to 145 °C for 20 min reversed the Diels–Alder linkages. The linear polymer was found to be recyclable at least four times and the crosslinked network was recyclable at least eight times.

Diels–Alder crosslinking materials have also been prepared from renewable resources. Reinecke and Ritter developed a dieneophile-modified unsaturated oligoester that formed branched networks when reacted with trisdienes and formed crosslinked networks when reacted with tetradienes.<sup>119</sup> Furfuryl amides and sorbic acid were both used successfully as dienes. No mention was made as to the reversibility of the network. Laita *et al.* were also interested in using the Diels–Alder reaction to develop novel polymers from renewable resources.<sup>15</sup> They prepared polyurethanes and acrylic copolymers bearing furan groups. Crosslinking with bismaleimides occurred; however, the retro-Diels–Alder reaction did not take place, ostensibly because of aromatization of the Diels–Alder adduct.

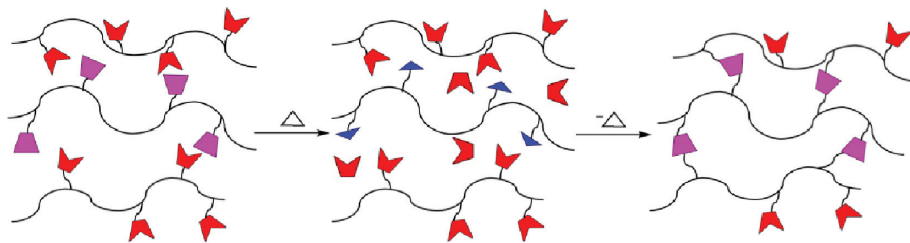
### 9.3.7 Smart Materials

A number of polymer networks have been designed that take advantage of the reversible nature of the Diels–Alder reaction to have a thermally controllable character. The change can be an optical property or conductivity or the formation of a new type of polymer network.

Dendrimers, repeatedly branched macromolecules, have been proposed for use as sensors and as drug delivery systems. Reversibly forming dendrimers are desirable for drug delivery because they can be designed to reach a desired target and, upon heating, break apart to release the chemical payload. Although the Diels–Alder chemistry was used previously to prepare dendrimers,<sup>63–65</sup> McElhanon and Wheeler were the first to develop a thermally reversible dendrimer.<sup>17</sup> Up to third-generation dendrimers were reported based on substituted maleimides and disubstituted furans as the dendrons. Dendrimers were observed to break apart upon heating and reform when cooled using <sup>1</sup>H NMR. In their work, the formation of Diels–Alder adducts was much slower than its cleavage.

Luo *et al.* prepared smart nonlinear optical (NLO) polymers with Diels–Alder-controlled crosslinks.<sup>41</sup> Organic NLO polymers are desirable for application in electro-optic devices with broad bandwidths and low drive voltages. However, they suffer from low thermal stability and solvent resistance, both problems that could be solved by crosslinking. Polymer chains were functionalized by maleimide and furan, with the maleimide initially protected by a furan. Figure 9.5 shows the reaction scheme for such a system. When crosslinking was desired, the system was heated to 125 °C for 30 min (deprotecting the maleimide) and subsequently cooled (forming the crosslinks between chains). The resulting crosslinked material retained approximately 80% of its electro-optic coefficient,  $r_{33}$ , value and was significantly harder and more thermally stable.

Thermoreversible fluorescence has been achieved by functionalizing chromophores with maleimide. Reacting maleimide-bearing chromophores with furan turned on the fluorescence, and the retro-Diels–Alder reaction was used to turn off fluorescence. Additionally,

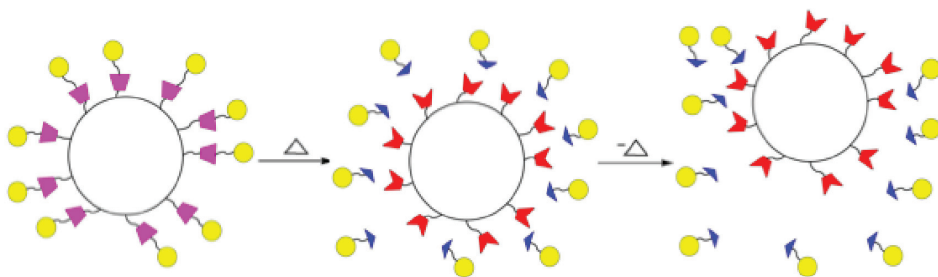


**Figure 9.5** Schematic of a polymer with thermally controlled crosslinking. When crosslinking is desired, the system is heated and dienophiles are unprotected, allowing them to react with diene-bearing linear polymers. Dienes are shown as notched trapezoids, dienophiles are shown as triangles and Diels–Alder adducts are shown as trapezoids.

reaction of the chromophore with furfuryl alcohol resulted in a self-organizing structure. At a low ( $1.0 \text{ mg mL}^{-1}$ ) concentration, spherical aggregates were formed, and at a high ( $10 \text{ mg mL}^{-1}$ ) concentration, dendrimers were recovered. Upon heating to  $75\text{--}80^\circ\text{C}$ , the structures disappeared, but would reappear after stirring at room temperature for 6 h.<sup>62</sup>

Kim *et al.* combined these two research areas and developed maleimide-functionalized NLO chromophores that react with polymers bearing pendant anthryl groups.<sup>120</sup> Both crosslinking and linear systems were synthesized, although crosslinked systems are more desirable for reasons mentioned previously. Changing the attaching mode of chromophores on the polymer controls the material's macromolecular architecture. No mention was made regarding reversibility of maleimide–anthryl linkages.

Stimuli-sensitive films are designed to respond to a specific stimulus, such as temperature, autonomously and in a useful way for the given application. Costanzo *et al.* developed a PEG film containing gold nanoparticles that ‘bloom’ to the surface upon heating.<sup>47</sup> Figure 9.6 is a schematic representation of this system's behavior. Migration of the gold nanoparticles destroyed weak long-range order within the film. Gold nanoparticles were functionalized with a diblock copolymer of maleimide-terminated polystyrene and furan-terminated PEG. Increased temperature cleaved the furan-terminated PEG from the gold nanoparticle and made the gold immiscible in the PEG film, causing gold migration.



**Figure 9.6** Diels–Alder functionalized particles with controlled dispersion. Upon heating, PEG ligands cleave from the particles, making them immiscible in the system and causing blooming and aggregation. Dienes are shown as notched trapezoids, dienophiles are shown as triangles and Diels–Alder adducts are shown as trapezoids.

Maleimide-functionalized gold nanoparticles were also prepared by Zhu *et al.* and used in the formation of monolayer protected nanoparticle (MPN) networks.<sup>91</sup> Like Costanzo *et al.*, Zhu *et al.* prepared maleimide-functionalized gold nanoparticles where the maleimide was initially protected with a furan-bearing group. Furan can be removed by heating to 100–110 °C for 12 h and subsequently washing. MPN networks were formed by mixing maleimide- and furan-functionalized gold nanoparticles. These networks, which appeared as large insoluble aggregates, broke apart and became miscible upon heating to 100 °C for 1 h. This reversibility was possible even after 30 cycles.

Costanzo and Beyer reported an optically active PEG film containing silica nanoparticles.<sup>48</sup> These silica nanoparticles were functionalized in a similar fashion to the gold nanoparticles from Costanzo *et al.* and dispersed throughout the PEG film. Upon heating, furan-bearing PEG ligands broke off from maleimide-functionalized silica nanoparticles. Silica nanoparticles then aggregated as a result of their immiscibility in PEG, changing the film from clear to opaque.

## 9.4 Conclusions

When developing a polymer network based on the Diels–Alder reaction, there are a number of parameters that must be considered, such as operating and reversing temperatures, concentration and location of Diels–Alder bonds, the type of Diels–Alder bonds, and base polymer material properties. These parameters, along with others that have been discussed, determine the kinetic, thermodynamic and thermomechanical behavior of the material. Although the Diels–Alder reaction is considered to be a classic click chemistry, there continue to be new and exciting applications of the Diels–Alder reaction to polymer networks. The range of dienes and dienophiles available as well as the extensive characterization of this reaction in the literature make the Diels–Alder reaction highly desirable for application in novel materials. However, to be able to fully exploit the reversible nature of the reaction in relation to polymer properties and functionality, more work is needed to understand the temperature-dependent equilibrium behavior of these systems, as well as the influence of diffusion limitation imposed by the macromolecular nature of the materials conceived.

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