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Study of high glass transition temperature thermosets made from the copper(I)-catalyzed azide–alkyne cycloaddition reaction

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Abstract

Thermal properties of polymers made from the copper(I)-catalyzed cycloaddition reaction between azides and alkynes have been investigated. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to measure the glass transition temperatures (T_g) of these materials. The polymers were found to have unusually high T_g values, up to 60 °C higher than the curing temperature. It has been shown that the increase of T_g was time dependant, thus, depending on the state of cure of the material.

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1. Introduction

Sharpless and colleagues published in 2001 an analysis of the most efficient chemical reactions that can be used to stitch organic fragments together to make complex functional molecules [1]. The authors argued that biological activity – the function of greatest concern to the organic synthesis community – should be easier to achieve by restricting synthetic operations as much as possible to such reactions, grouped under the name "click chemistry". While something of a controversial proposition in organic synthesis and medicinal chemistry, the use of a limited number of supremely reliable bond-forming methods to achieve sophisticated function is of course the foundation of polymer science. We seek to introduce into polymer chemistry some of the click reactions that have been explored thus far only in the context of drug discovery to broaden the base of connections available to make functional materials.

The copper(I)-catalyzed cycloaddition reaction between organic azides and terminal alkynes [2,3] to make 1,4-disubstituted 1,2,3-triazoles has emerged as the most versatile click reaction for making connections to biological molecules [4–8] and for the discovery of biologically-active compounds [9–11]. The reaction is useful in biological settings for two main reasons: the azide and alkyne components are largely unreactive with biological molecules (and therefore selectively reactive with each other), and the product triazole can interact with biological structures in several noncovalent ways while being at the same time extraordinarily stable. The azide–alkyne cycloaddition has also rapidly captured the attention of investigators in materials science for similar reasons [12–21]. The synthesis of the linear polymer **3** is illustrative of a condensation polymerisation involving the azide–alkyne cycloaddition (AAC) reaction, as shown in Scheme 1. We have previously reported that multivalent azides and alkynes, when deposited between surfaces containing metallic copper, are crosslinked by Cu(I)-mediated triazole formation to give strong adhesion of one surface to the other [22]. Here we report the results of follow-up studies on two of these systems as well as the properties of the analogous polymers made in bulk. An unusual relationship between glass transition temperature and curing temperature has been established.

1,2,4-Triazoles are widely used in corrosion inhibitors and adhesion promoters on copper or copper based products

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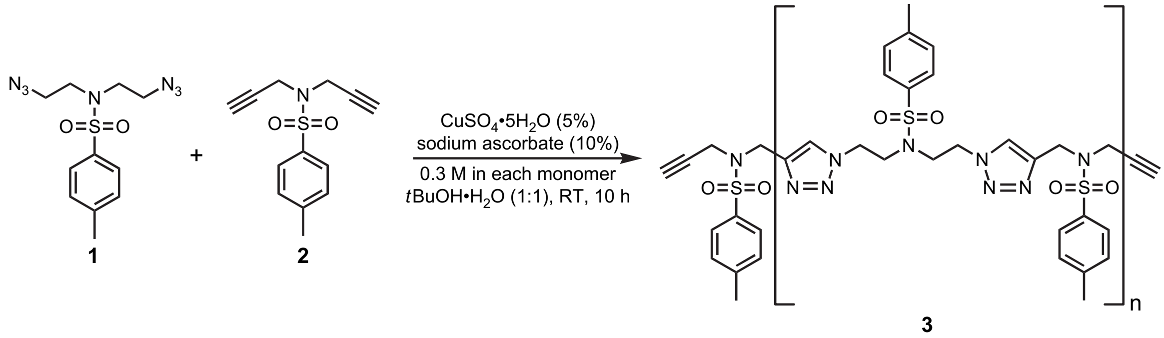


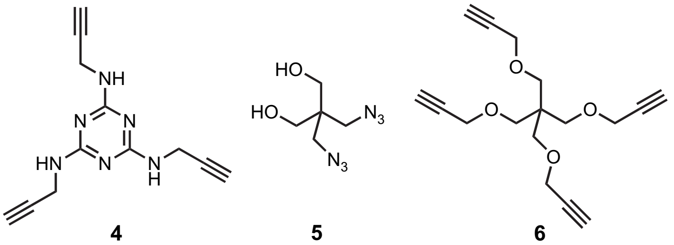
Scheme 1. Synthesis of a main-chain triazole polymer using the azide–alkyne cycloaddition reaction.

[23–29]. The poor durability of copper in oxidative environments derives from the inability of copper oxide to protect the surface toward continued corrosion. Polymers incorporating 1,2,4-triazoles act as a stabilizing inert film by covering the vulnerable oxide layer [28]. With the exception of benzotriazoles, the 1,2,3-triazole isomer is poorly represented in the adhesives and coatings literature because of the difficulty of its synthesis prior to the development of the Cu(I) catalytic procedure. However, our work provides evidence that 1,2,3-triazoles have good affinity for metallic surfaces and are far more stable than 1,2,4-triazoles to attack by other chemical entities. We therefore believe that 1,2,3-triazole-based materials have advantageous properties for high-performance metal coatings and adhesives. Since Cu(0)-containing surfaces can supply Cu(I) ions (presumably by comproportionation with Cu(II) derived from air oxidation), the azide–alkyne cycloaddition reaction is "self-starting" on such surfaces (Scheme 1).

2. Experimental

2.1. Polytriazole adhesives: bulk polymerisation

Quantities of **1** and **4** (3:2 molar ratio) or **5** and **6** (2:1 molar ratio), each providing an equivalent concentration of azide and alkyne groups, were stirred in THF (tetrahydrofuran, 99.9%, high-performance liquid chromatography (HPLC) grade, inhibitor-free, from Sigma–Aldrich) for at least 30 min until the solution appeared to be homogeneous. Copper(I) iodide (99.999% from Aldrich) was added as a fine powder (10% in weight) to the mixture over 2 min with vigorous stirring. The soluble Cu(I) complex $[Cu(CH_3CN)_4]PF_6$ was used as catalyst (10% in weight) for reactions of **5** and **6**. The THF solution was immediately spread with a Pasteur pipette on the surface of the brass plates (cleaned just before use with acetone and toluene). Before sticking the plates together, the solvent was allowed to evaporate for between 10 s and 3 min.



4 5 6

Fig. 1. Azide and alkyne compounds used in the reactions.

Samples prepared between copper or brass plates were cured at three different temperatures (room temperature, 50 °C, and 100 °C) and were tested after curing times varying from 2 to 30 days. Samples for differential scanning calorimetry (DSC) measurements were obtained by prying apart the glued plates and scraping the sample off the copper surface just prior to analysis.

2.2. Analytical methods

Modulated differential scanning calorimetry (MDSC) was performed with a DSC Q100 instrument (TA Instruments, Inc.) in modulated mode to separate the reversing heat flow (characterizing the glass transition temperature, T_g) and the non-reversing heat flow. Non-hermetic aluminium pans were used. The temperature was swept from 0 °C to 250 °C at a rate of 3 °C/min and a modulation period of 60 s. T_g values were determined using the midpoint method integrated in the software (Universal Analysis).

Dynamic mechanical analysis (DMA) was performed on samples made by joining two rectangular thin brass shims (35 mm long, 10 mm wide, 0.06 mm thick) with the polymer in between. The thickness of the adhesive between the shims varied from 0.07 mm to 0.27 mm. Measurements were performed with a DMA Q800 instrument (TA Instruments) using single cantilever clamps. Samples were held horizontal by two clamps with a sample length of 17.5 mm between them. One clamp was fixed, whilst the other applied a vertical displacement the sample. Samples were subjected to a temperature ramp from −20 °C to 200 °C at a rate of 3 °C/min. The clamp displacement was 50 μm with a frequency of 10 Hz with a maximum strain in the sample of 1.21×10^{-4}. The glass transition temperature was calculated as the mean of the loss modulus peak and the tan δ peak.

3. Results

3.1. Thermal properties of mixture *1 + 4*

The mixture of diazide **1** and trialkyne **4** was chosen as a representative of an adhesive of average strength, as determined in our preliminary measurements [22]. The cross-linked polymer was prepared by polymerisation in solution as well as by bulk (solvent free) polymerisation between copper-containing plates. MDSC measurements on the solution prepared material showed an endothermic peak on the non-reversing heat flow curve at approximately 50–70 °C (Fig. 2). Similar results were obtained on the bulk polymerised material. When a sample of bulk polymerised material was crushed into powder and then heated at 200 °C for 24 h, MDSC data recorded immediately thereafter showed no such endothermic peak. Analysis every few days of a sample stored at room temperature in air then showed the endothermic peak growing in intensity as a function of time (Fig. 3). The T_g of the material (as measured by MDSC) was also found to decrease in a similar time-dependant fashion. The endothermic peak is therefore probably due to the evaporation of water that had absorbed into the hygroscopic material, with the residual (that remaining at temperatures above 180 °C) water acting as a plasticizer in its effect on the glass transition.

Preparation of an adhesive between copper plates was usually performed using THF solutions of the monomers. Evaporation of the solvent was monitored by the measurement of weight under the typical conditions of curing between brass cantilever plates at room temperature (Fig. 4). A rapid loss of solvent was noted even though the adhesive mixture was exposed to air only at the plate edges. Approximately 25% of the THF was lost in the first hour and 94% evaporated after 3 days. A final value of 97% (leaving 3% solvent remaining) was achieved after 1 week. Hence the polymerisation process that occurs over several days may be considered to be a process in the bulk rather than in solution.

MDSC analysis of samples made between copper plates without additional catalyst shows that curing was quite slow compared to the reaction in solution, as expected (Fig. 5). The T_g value of the material made from **1** + **4** attained a value of up to 60 °C above the curing temperature after 10–15 days, and this behaviour of a T_g well above the curing temperature was observed for three curing temperatures (RT, 50 °C, and 100 °C). The results of DMA analysis of the adhesive formed by spreading the same mixture of monomers (**1** + **4**) between brass foils is shown in Fig. 6. T_g values determined in this manner followed the same trend as those measured by MDSC. Judging by these T_g profiles, the polymer reached a curing level of approximately 90% after 4 days when

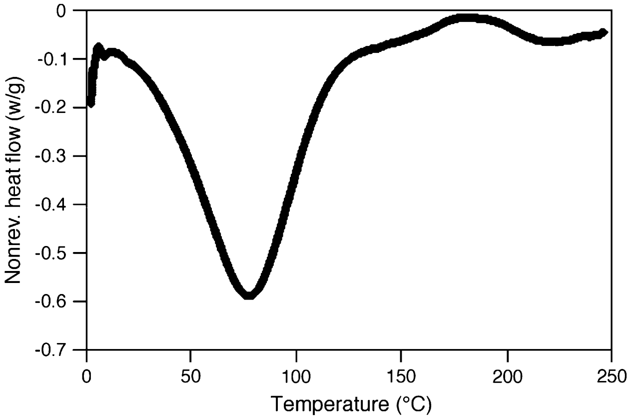


Fig. 2. MDSC analysis of the polymer prepared from **1** + **4**, prepared in solution at 60 °C. The non-reversing heat flow shows an endothermic peak at 70 °C.

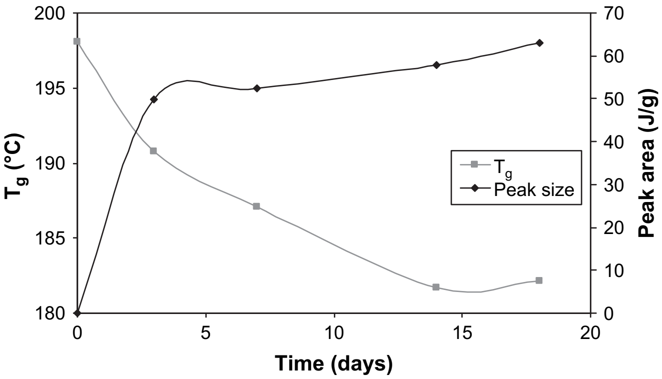


Fig. 3. Evolution of the MDSC endothermic peak size and T_g with the time of exposure to air.

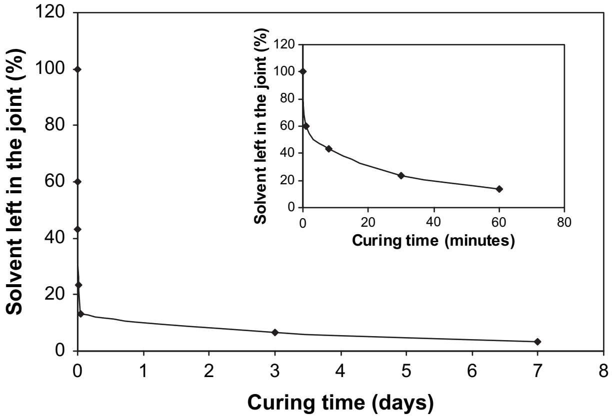


Fig. 4. Solvent evaporation as a function of curing time for a typical cantilever adhesive.

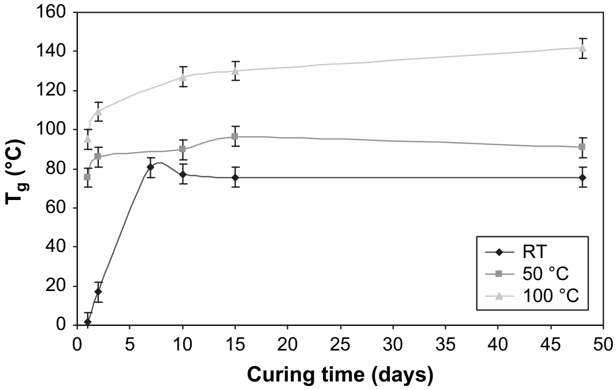


Fig. 5. MDSC of the **1** + **4** adhesive cured between Cu plates as a function of curing time (room temperature; glued samples were broken apart approximately 1 min before MDSC analysis to avoid changes in behaviour caused by water absorption).

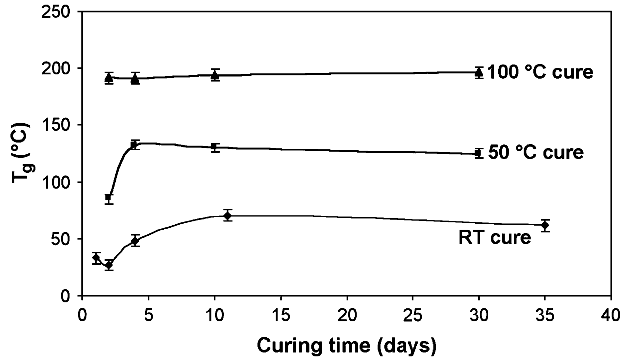


Fig. 6. Evolution of T_g with curing time of **1** + **4** at different curing temperatures determined by DMA single cantilever measurements.

incubated at 50 °C and 100 °C, but required 10 days for curing at room temperature. The drop in apparent T_g after 35 days was probably due to the plasticizing effect of adsorbed water.

Thus, polymerisation of **1** + **4** (solvent free between brass plates) produced materials with unusual T_g values significantly higher than the curing temperature. This is very unusual, as discussed below, for bulk (solvent free) polymerisation reactions.

3.2. *Thermal properties of mixture* **5** + **6**

The thermal properties of polymers made from monomers **5** and **6** were investigated in the same manner, giving similar results. Thus, Fig. 7 shows the evolution of the T_g as a function of the curing time for materials made at 50 °C and 100 °C. At room temperature, curing occurred to only low T_g after 15 days, and so was not further analysed. As with **1** + **4**, the final T_g for **5** + **6** is reached after 10 days of cure at elevated temperature. At 50 °C, this final T_g was found to be 60 °C higher than the curing temperature, and at 100 °C, T_g increased to 48 °C above curing temperature.

4. Discussion

The copper(I)-catalyzed AAC reaction between diazides and trialkynes is expected to produce highly crosslinked polymers which can be considered as thermosets. When a thermoset undergoes polymerisation and crosslinking in the absence of a solvent its glass transition temperature increases with degree of polymerisation until either (i) it becomes fully cured with a glass transition temperature less than the curing temperature or (ii) the material vitrifies before fully cured and the rate of reaction becomes diffusion controlled and extremely slow. In the latter case the final glass transition temperature, at least for epoxies, is between 10 °C and 25 °C above the curing temperature [30,31]. In physically large items, apparently higher T_g's have often been observed but that is just because the reaction exotherm increases the temperature of the material being cured to significantly above the applied temperature.

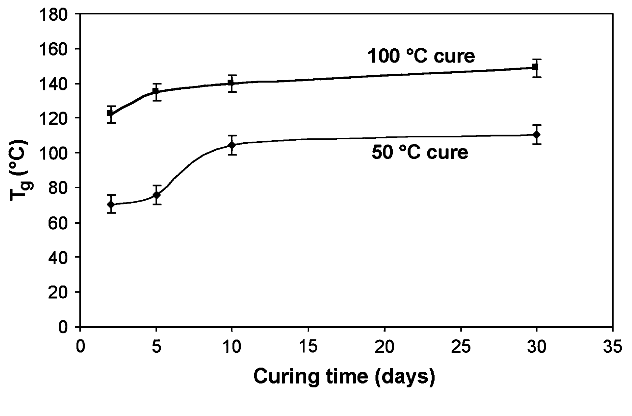


Fig. 7. Evolution of T_g with curing time of **5** + **6** at different curing temperatures as determined by DMA single cantilever measurements.

Larger differences between the T_g and the curing temperature have been reported, in one case in an epoxy [32], however, it has been suggested that the high T_g in this case was the result of thermal degradation rather than curing [33]. A glass transition temperature 40 °C above the cure temperature was recently obtained by the use of reactive additives in a polyarylene, however, there was no discussion of the curing mechanism [34]. Glass transition temperatures 70 °C [33] to 100 °C [35] above the cure temperature have been reported in highly crosslinked, radically polymerised systems cured by photopolymerisation. It was suggested that the large differences between T_{cure} and T_g were obtained in these systems because (i) they cure by a chain growth polymerisations and (ii) very inhomogeneous networks were formed. More diffusion is expected in the vitreous state in chain growth polymerisations because a considerable amount of monomer can remain up to high conversions whereas that does not happen in chain growth polymerisations. In addition it was suggested that the active radicals may maintain a relatively high mobility in the glass through hydrogen transfer thus the reaction continues to occur deep into the glassy state. Network inhomogeneity is believed to increase T_g–T_{cure} because regions of high mobility will still exist in the glass permitting radicals, monomers and pendant double bonds to still diffuse and react.

The materials described here have a final T_g that is up to 50–60 °C higher than the curing temperature, well above the normal range of 10–25 °C seen in step growth polymerisation systems. Furthermore, this phenomenon appears to be general: the core structures of monomers **1** and **4** (aromatic rings) vs. **5** and **6** (pentaerythritol) (Scheme 1, Fig. 1) are quite different, and yet the T_g–T_{cure} relationship is similar. Other combinations of multivalent azides and alkynes linked by Cu(I) catalysis have also been found to behave similarly. Under normal circumstances, T_g of some thermosets can be up to 20 °C higher than the curing temperature due to bulk exothermic effects, the reaction exothermicity raising the temperature of the environment above that of the external medium as discussed above. The adhesive samples were extremely unlikely to experience bulk heating, since they were thin films (average 0.12 mm thickness) formed in slow polymerisations between metal sheets. Note, too, that such a high T_g polymer takes from 2 to 10 days to reach its final glass transition temperature when prepared on copper-containing surfaces with no added catalyst. At this stage the amount of solvent is very low.

This suggests that the curing reaction still proceeds even if the material is glassy and not much chain or monomer mobility is possible.

In the system described here, unlike the situation described in Ref. [35], the G′ and tan δ peaks are not unusually wide, so the large difference between T_{cure} and T_g cannot be explained by inhomogeneity of the network. Instead, the mechanistic nature of the AAC process may be at least partially responsible for the observed high T_g values by creating chain crosslinks with unusual facility. Triazoles have good thermodynamic affinity for Cu(I) ions and yet the Cu–triazole interaction is kinetically labile. Cu ions should therefore be able to move readily from one triazole binding site in the developing network to another, even when the network is in the glassy state, in a similar way to radical diffusion in addition polymerisations. Cu–triazole complexes are also known to be good catalysts for the AAC reaction [36]. These factors combine to make it possible for Cu ions to migrate through the structure to create local "hot spots" of catalytic reactivity, especially in areas of the polymer matrix in which multiple triazoles have already been formed. The liberation of energy that attends every azide–alkyne cycloaddition event (exothermic by approximately 50 kcal/mol) may also induce increased local motion of polymer chains in the vicinity of the catalytic hot spots.

The nature of the triazole unit may also be important. We have found in previous work that linear polymers assembled from diazides and dialkynes, such as **3**, are unusually brittle and poorly soluble, although their T_g values are reasonably close to their curing temperatures [22]. The mechanical and solubility properties of these linear condensation polymers are likely due to the properties of the triazole unit in the main chain of such materials. 1,2,3-Triazoles have large dipole moments, good hydrogen bond accepting capability, and a pseudoaromatic nature that allows for π-stacking. Each of these factors can contribute to strong noncovalent interactions, and we suggest that associated domains are thereby formed very easily, leading to brittle materials in the case of the linear polymers and perhaps to associated domains of unusual stability during the formation of crosslinked networks from $\mathbf{1}+\mathbf{4}$. 1,2,4-Triazoles are quite common in the literature of metal coatings and adhesives [26,28,37], but no reports of unusually high T_g values have been made for these systems. This is significant because 1,2,4- and 1,2,3-triazoles share an affinity for binding metal surfaces through N–σ donor interactions, but 1,2,3-triazoles have much higher dipole moments than that of the 1,2,4-isomers.

5. Conclusion

High glass transition temperature thermosets have been formed between copper or brass plates by the copper(I)-catalyzed AAC reaction of diazides and a tri- and quad-alkyne. The material can show a T_g up to 50–60 °C higher than the curing temperature after curing for several days. This behaviour can be seen for different curing temperatures from RT to 100 °C. Solvent evaporation is not an issue as the solvent evaporates very quickly leaving an insignificant amount in the adhesive joint. The materials are unusual as they continue to react, showing some local mobility, in spite of being in the glassy state. We can then assume that the curing rate of the sample is mainly dependant of the curing time and temperature. From a practical point of view, such materials may be useful as corrosion inhibitors or adhesives on copper or copper based substrates.

Acknowledgements

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