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## COMMUNICATION

## Self-Healing and Shape Memory Capabilities of Copper-Coordination Polymer Network

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**A novel smart material with excellent shape memory and high self-healing capabilities has been developed through metal ion coordinating polymer. The copper-coordination polymer network (Cu-PIE) is formed via the isonicotinate moiety of isonicotinate-functionalized polyesters (PIE) covalently cross-linking with copper ions.**

Shape memory polymers (SMPs) have an ability of changing their shape and recovering to their original shape by application of an external stimulus. They receive more and more attention for their potential applications in sensors, actuators and biomedical devices.<sup>1-3</sup> However, the application of conventional SMPs with single function is limited because they cannot meet the requirement of complex and variable environment in actual applications. Currently, the multifunctional SMPs have become a hot topic, which possess shape memory property and other functions, such as biodegradability,<sup>4-7</sup> drug release<sup>8</sup> and self-healing property.<sup>9-11</sup>

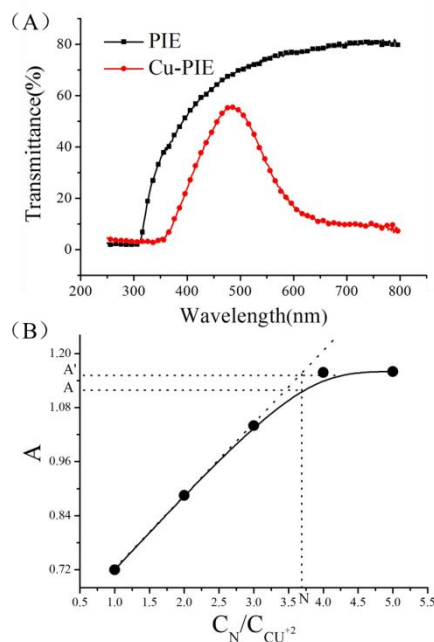
Self-healing is increasingly becoming an important concept in designing smart materials. Self-healing polymers can repair themselves and in turn recover to their original shapes after damage.<sup>12-14</sup> Nowadays, the self-healing approaches generally include extrinsic and intrinsic self-healing.<sup>15-20</sup> The extrinsic self-healing takes effect by inserting microcapsules loaded with healing agents into polymer matrix. The healing agents can be released when the materials cracks, and heal the crack. However, this kind of self-healing polymers can be healed only once at the same location due to the exhaustion of the healing agents. The intrinsic self-healing is capable of healing cracks by the polymer themselves without additional healing agent. To date, reversible physical or chemical interactions in polymer matrix have been utilized for this intrinsic self-healing polymers, containing alkoxyamine moieties,<sup>16,21</sup> Diels-Alder interactions,<sup>22</sup> thiuram disulfide units,<sup>23</sup> coumarin derivatives,<sup>24,25</sup> acylhydrazone bonds,<sup>26</sup> disulfide links,<sup>27</sup> hydrogen bonding,<sup>28</sup>  $\pi$ - $\pi$  stacking,<sup>29, 30</sup> ionomers,<sup>31</sup> etc. In contrast to the extrinsic self-healing, the intrinsic self-healing can allow for repeated healing. Achieving a high healing efficiency to polymer matrix is still a great challenge.

In terms of the structure of SMPs, they consist of fixity phase and reversible phase. In general, cross-linked networks which contain chemically cross-linked structure and physically cross-linked structure constitute the fixity phase. Metal-ligand coordination as a kind of covalently cross-linked structure can be also used as fixity phase in shape memory system.<sup>32-34</sup> The metal-ligand coordination polymers are generally compounds containing the coordinative interaction of metal ions and the charged or neutral organic ligands.<sup>35</sup> Among these ligands, reactive pendant isonicotinic acid group is widely used as a kind of pyridinium-type ligands.<sup>36</sup> Copper ion is an

excellent candidate for the coordinative interaction of the metal-ligand coordination polymers due to the low cost and good accessibility.

In our previous work, we synthesized a novel isonicotinate-functionalized polyester (PIE) via classical melt-condensation polymerization, and found that the pendant of the pyrazinamide groups on the polyester side chains of this polymer could be coordinated with Ag ions to form a physically cross-linked network, which possessed antibacterial action and shape memory capabilities.<sup>37</sup> In this study, through a further investigation of this polymer, we found that the isonicotinate moiety could be readily coordinated with copper ions to form copper-coordination polymer network (Cu-PIE), and this network exhibited excellent thermo-induced shape memory effect and high self-healing property. However, the Ag-PIE network did not present a self-healing effect. By comparison to the self-healing approaches currently reported, the metal-ligand coordination is simpler and easier to operate, moreover the healing can be repeated. This multifunctional polymer with combination of shape memory and self-healing properties has a great potential application in surface self-repairing of biomedical devices.

The chemical structure of PIE and its isonicotinate moiety easy coordination with Ag ions were confirmed in our previous work.<sup>37</sup> Here, this polymer was coordinated with copper ions to form copper-coordination polymer network (Cu-PIE) and its chemical structure was measured by FT-IR and UV-vis, respectively. In the FTIR spectrum of the Cu-PIE (**Figure S1** in SI), we can clearly find that in contrast to the characteristic absorptions of C-N stretching vibration at 1450 and 1490  $\text{cm}^{-1}$  for pure PIE, the red shift occurs for Cu-PIE due to the ligand coordinating with Cu ions. To further confirm the successful synthesis of the coordination polymer, solid UV-vis was employed. From **Figure 1A** we can find that there is a maximum transmissive peak at 490 nm in Cu-PIE but not in pure PIE, which can be owing to the Cu ions coordination. Additionally, the stability of the supramolecular polymer based on metal-ligand interactions plays a crucial role in determining its functions. Consequently, the stability constant (K) of Cu-PIE was measured to evaluate the stability of this polymer network. From **Figure 1B**, it can be achieved that the stability constant  $\lg K$  of copper-coordination polymer is 6.24, which is almost in accordance with copper-pyridine ligand's 6.54, suggesting that the structure of the copper-coordination polymer network is highly stable.



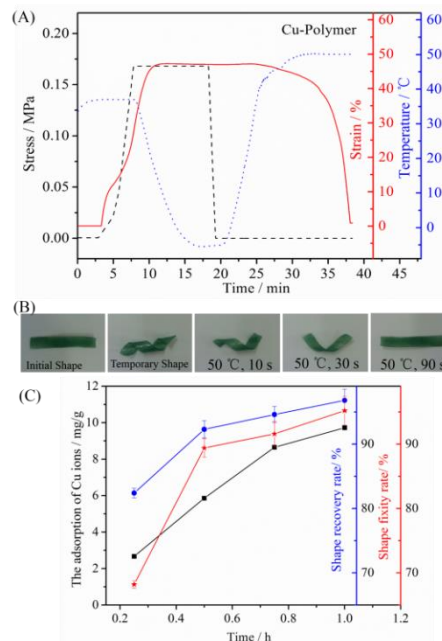
**Figure 1.** (A) UV-vis curves of PIE and Cu-PIE; (B) Stability constant of Cu-PIE polymer.

To confirm the amount of adsorbed Cu ions in Cu-PIE, TG analysis was carried out as shown in **Figure S2** in SI. By comparison to pure PIE, the temperature of decomposition for Cu-PIE increases, and the amount of adsorbed Cu ions in this polymer network is approximately ~ 5.93%, which was calculated from the weight loss curve. The result demonstrates that the polyester coordinated with Cu ions possesses a better stability. From the thermal transition temperature of the Cu-PIE in DSC curve (**Figure S3** in SI), we can see that the Cu-PIE holds a wide glass transition temperature region from ~ 20 °C to ~ 100 °C similar with pure PIE.

The dynamic mechanical behavior depending on temperature is an important mode in predicting the shape memory property and providing information for shape fixity and recovery.<sup>38</sup> **Figure S4** in SI shows the storage modulus and tan delta curves of the PIE and Cu-PIE. When at lower temperature, the Cu-PIE has a higher storage modulus (1770 MPa) than that (950 MPa) of PIE. And from the curves of tan delta values versus temperature, we can also observe that the Cu-PIE exhibits a wide glass transition temperature. A great difference of modulus between rubbery state and glassy state also demonstrates that Cu-PIE possesses an excellent shape memory effect.<sup>39</sup> From the variation of tan delta value, we can find that the Cu-PIE has a higher transition temperature from 30 °C to 75 °C than the transition temperature of the pure PIE, which is consistent with the result of DSC analysis. The wide glass transition temperature region can provide the deformed and recovery temperature of the shape memory process.

Thermo-induced shape memory effect of the Cu-PIE was further investigated by DMA with a controlled force mode in **Figure 2A**. From the quantitative result of DMA analysis, it can be seen that the Cu-PIE exhibits an excellent shape memory effect, both the shape fixity ratio and recovery ratio remain above 95% calculated from the equations (1) and (2). Moreover, from the macroscopic shape memory process of Cu-PIE in **Figure 2B**, we can also observe that the Cu-PIE has high shape fixity ratio and shape recovery ratio. In this shape memory system, the pyrazinamide groups as a good ligands of PIE can easily coordinate with Cu ions to form a cross-linking structure as

shown in Figure 4F. In the process of shape memory, the cross-linking structure can act as the fixity phase to provide the elasticity for recovering their initial shape. The polyester molecular chains acts as the reversible phase for the formation and fixation of the temporary shape.



**Figure 2.** Shape memory properties of Cu-PIE measured by DMA (A); shape memory fixing and recover process of Cu-PIE (B); shape fixity ratio and shape recovery ratio versus different amount of absorbed Cu ions (C).

The Cu ions concentration coordinated with polymer was further optimized to achieve the best shape memory effect. The accumulated amount of absorbed Cu ions in polymer matrix at the designated time was analysed by Atomic Absorption Spectroscopy (AAS). From **Figure 2C**, it can be observed that after immersed in CuSO<sub>4</sub> solution (4 g/L) for 60 min, the amount of absorbed Cu ions almost gets to the maximum value of approximately 9.2 mg/g (Cu ion/PIE). To evaluate the stability of Cu-PIE, the release of Cu ions from the Cu-PIE were measured in water at 25 °C and 37 °C respectively by Inductively Coupled Plasma (ICP). From **Figure S5** in SI, we can find that the release speed at 37 °C is faster than that at 25 °C, but the accumulated released amount in 24 h only reaches to 0.60 ppm at 37 °C, which is far lower than the absorbed Cu ions amount, further confirming that the Cu-PIE has good stability in water.

Previously we found that the concentration of Ag ions in polymer matrix has a great influence on shape fixity ratio and shape recovery ratio of Ag-coordination polymer network.<sup>37</sup> Herein, we acquired a similar result that both the shape fixity ratio and the shape recovery ratio of Cu-PIE are dependent on the concentration of the absorbed Cu ions (**Figure 2C**). The reason can be ascribed to the fact that there are many isonicotinate side groups on PIE backbone, and they need to coordinate with enough Cu ions to form a polymer network with a high cross-linking density. For this supramolecular polymer, the high cross-linking density and stable coordination structure are necessary in achieving excellent shape memory function.

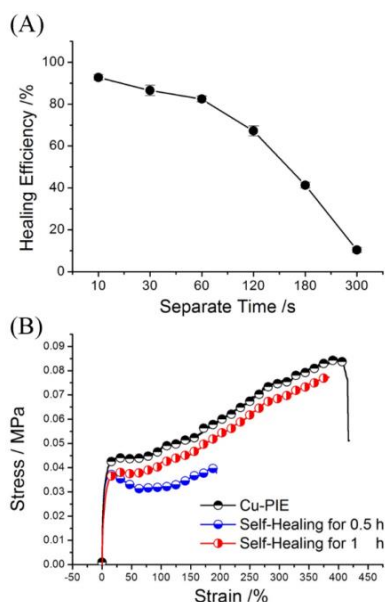
The self-healing properties of Cu-PIE were investigated by separated time, healed time and fracture area. The PIE is a hydrophilic polymer and its molecular structure determines the rigid structure of PIE. From DSC curve, we know that PIE shows a glass state at room temperature (22 °C). Firstly, we investigated the self-healing property

of PIE containing different amount of water at 45 °C higher than glass transition temperature. From **Table S1** in SI, it can be seen that with the water content increasing to 5%, the self-healing efficiency increases but decreases with a larger amount of water content (10%). In particular, when the water content is 5%, the self-healing efficiency for 1 h is the highest and approximately  $91.89\% \pm 1.28\%$ . The reason of the self-healing property varied with water content can be explained by the structure of the polymer. Since the polymer has a rigid structure bearing pyridine ring on the side chains, the flexibility of which would be increased by penetration of water molecule. However, the irreversible slippage of polymer molecular chains would happen resulted from excess water content. Therefore, it is necessary to control suitable water content. Thus, the temperature of 45 °C is selected for the self-healing temperature, and 5% water content is optimized for the investigation of self-healing property of Cu-PIE. When water content reaches to 10%, polymer molecular chains prone to slipping, resulting in a lower self-healing efficiency.

Moreover, the self-healing properties of Cu-PIE were investigated by fracture area as shown in Figure S7, the results demonstrated that the rod-like Cu-PIE which possessed a bigger fracture area needs a longer self-healing time.

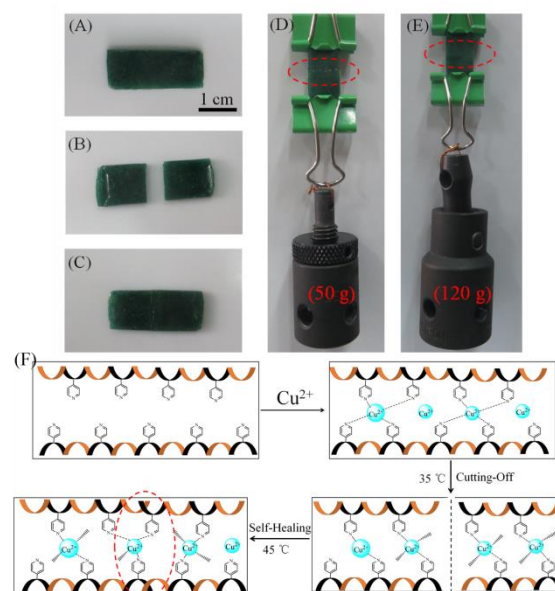
Figure 3A shows the healing efficiency of Cu-PIE under different separate time. With increasing separate time, the healing efficiency decreased due to the longer separation of the two cut surfaces. Subsequently, a nomenal self-healing of the materials in the cut surfaces would take place with the increase of separate time, causing the decrease of self-healing groups once the two cut surfaces contacted. As a result, the self-healing property would be weakened. It has been reported that most of hydrogel's self-healing ability remains at a separation time less than 1 h.<sup>40</sup> Here, when the separation time is less than 10 seconds, the self-healing efficiency remains more than 90%.

Figure 3B shows the fracture stress of different samples treated with different healed time. These data also reflect the high self-healing ability of Cu-PIE. With increasing healed time, the healing efficiency increases. After 1 h healing, the maximum tensile strength of the self-healed Cu-PIE is close to that of the original Cu-PIE, and the healing efficiency reaches to approximately 90.35%<sup>41</sup>.



**Figure 3.** Healing efficiency versus different separate time (A); Self-Healing property measured by Micro-tensile method in different time (B).

**Figure 4A-E** shows the self-healing process of Cu-PIE at 45 °C. The two cut surfaces were put together rapidly in alignment to have their freshly created fracture surfaces and stayed at 45 °C for 1 h (Figure 4B). It can be observed that the crack line in bulk almost disappears (Figure 4C) and the material recovers original shape (Figure 4A), and the healed Cu-PIE can bear a mechanical force in a weight of 50 g and 120 g (Figure 4D, E). The results indicate that Cu-PIE possesses high self-healing property.

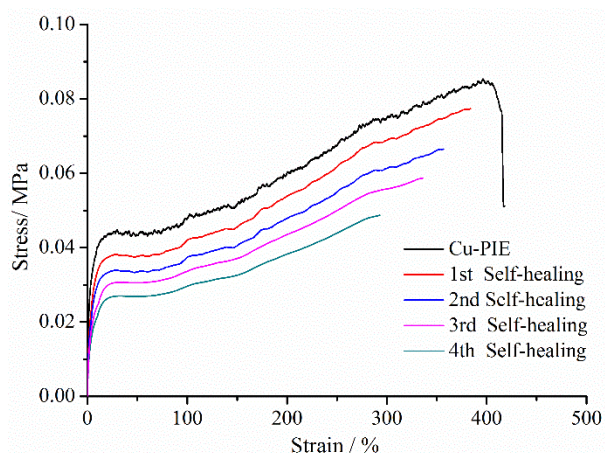


**Figure 4.** The self-healing property of Cu-PIE at 45 °C (A-E) and mechanism of the self-healing property of Cu-PIE (F).

In this copper-coordination polymer network, the N atoms of the pyrazinamide groups on the polyester side chains are coordinated with Cu ions to form supramolecular cross-linked structure as shown in Figure 4F. From the discussion mentioned above, we know that the Cu-ligand with the N atoms is highly stable in water. During the shape memory process, the cross-linked structure acts as fixity phase, and the polyester molecular chains can be looked as reversible phase. In this system, the performance of shape memory is mainly dependent on the stability of the cross-linked structure, which is mainly influenced by the cross-linking density. In self-healing process, the Cu-PIE sample was firstly cut apart at 35 °C; immediately the two cut surfaces were put together in alignment at 45 °C to perform the self-healing. The disappearance of the interface formed by the contact of the two cut surfaces is owing to the restructuring of the coordination bonds and the rearrangement of polymer molecular chains. For pure PIE polymer, there does not exist metal-coordination network, consequently no self-healing function can be found. For Ag-PIE polymer network, the self-healing efficiency is poor, which can be ascribed to the unstability of the Ag-ligand. Therefore, this copper-coordination polymer network can be extended to other systems containing stable metal-coordination bonding with polymer molecular chains.

Moreover, the healing repeatability of the Cu-PIE has been investigated as shown in **Figure 5**. From the results of Figure 5, the first, second, third and the fourth healing efficiency could reach 90.35%, 73.14%, 68.37% and 57.24%, respectively. This indicates that the Cu-PIE possess a good healing repeatability.





**Figure 5.** Healing efficiency versus different cutting times.

In summary, we developed a type of novel copper-coordination polymer network via a simple strategy, and this polymer network displayed excellent shape memory and high self-healing functions under a mild condition. In this polymer network, the pyrazinamide groups located in polymer side chains provide a ligand effect with the absorbed Cu ions and in turn endow the polymer with shape memory function. The self-healing property mainly resulted from the restructuring of the coordination bonds and the rearrangement of polymer molecular chains on the cut surfaces. By comparison to the self-healing approaches currently reported, the metal-ligand coordination is simpler and easier to operate, moreover the healing can be repeated. This strategy can provide a platform to design and engineer new smart materials.

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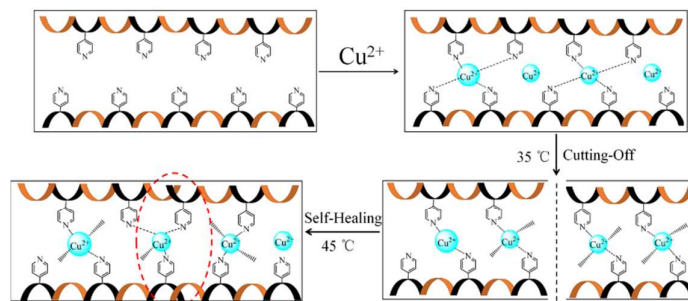
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## Notes and references

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A table of contents entry



A copper-coordination polymer network displays excellent shape memory and high self-healing functions under a mild condition.