CRYSTALLINE POLYMERS WITH MENDABILITY

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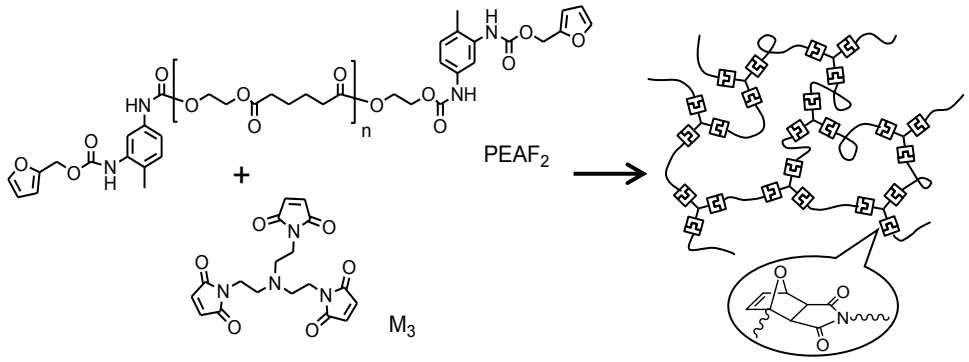
ABSTRACT

Materials with ability of repairing cracks either autonomously or by activation with some external stimuli have attracted great interest in recent years. Repairing ability offers extension of working life and enhancement of safety performance of polymer materials. One approach to obtain repairable polymers is the use of dynamic bonds such as reversible reaction and intermolecular interaction. When fractured surfaces are brought into contact, the dynamic bonds are potentially regenerated across the rupture. The dynamic bonds can fully reproduce molecular structures of the materials after damage. The polymer systems that exploit the dynamic bonds for crack repairing are sometimes referred to as being mendable. Mending mechanism is less workable in rigid polymers with fewer functional groups because of the lower collision frequency of the polymer chain. Therefore, the density of the functional groups and the molecular mobility of the materials are important for mendabiliy design. In previous papers, mending in crystalline or glassy polymers has been achieved by being swollen it by solvent and by raising the temperatures above the glass transition or melting temperature.

We are developing functional polymers by using dynamic bond. Our materials are made of telechelics of crystalline polymer with molecular weight ≈ 10^3, which are chain-extended or cross-linked by dynamic covalent bond or intermolecular interaction. The reversibility of the dynamic bond contributes to the good recyclability of these polymers [1,2] and thermo-responsible soft-hard transition [3,4]. In this paper, the remendability of this type of dynamic network polymers will be discussed. We will show that even with the crystalline nature, mending process can be effectively promoted by controlling the crystallization of the materials.

A network polymer is made from a furyl-telechelic prepolymer, $PEAF_2$, and a tris-maleimide linker, M_3 (Scheme 1) [5]. Cross-links in the polymers are given by reversible Diels-Alder (DA) reaction between furan and maleimide. Similar to the several different systems shown in previous papers, the reversibility of this DA reaction gives remendability to this network polymer. Damaged $PEAF_2M_3$ was



Scheme 1: Network polymer from $PEAF_2$ and M_3.

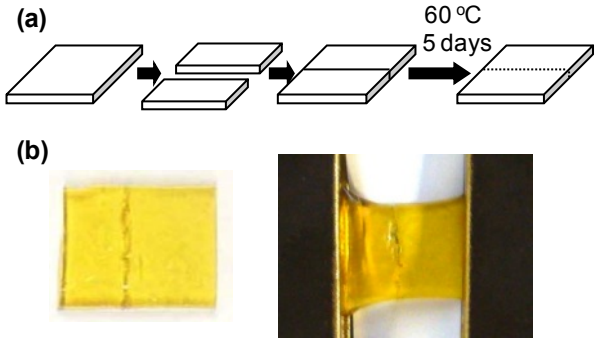


Figure 1: Mending behavior of $PEAF_2M_3$. (a) Mending treatment: a strip of $PEAF_2M_3$ with 1 mm thick was cut into two pieces. Immediately after that, the cutting surfaces were placed in contact with each other and kept at 60 °C for 5 days. (b) Photo images of mended $PEAF_2M_3$ in (left) relaxed and (right) stretched states.

repaired in the melt (Figure 1). Further, when the sample was melt by a prompt thermal stimulus, immediately followed by cutting and re-contacting at room temperature, repairing of the sample was observed. Though the mechanical properties of the repaired sample were much less than the original uncut sample, remending was apparently proceeded at room temperature. The crystallization of $PEAF_2M_3$ is relatively slow. The supercooled liquid state was kept for a few days at room temperature. The molecular mobility of $PEAF_2M_3$ in the supercooled liquid might promote the forward DA reaction between the cutting surfaces, resulting in the mending.

We also prepared telechelics end-functionalized with hydrogen bonding units [6]. By choosing the bond that connects the parent polymer and hydrogen bonding units, the crystallization rate of the polymer could be significantly slowed down. When the sample was cut, the degree of crystallinity at the cut surface is decreased by frictional heat. The low crystallinity was kept for a long period during which the free hydrogen-bonding units, which are generated at the cut surface by cut, associate again, resulting in the enhancement of self-healing ability of this crystalline polymer.

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