

# A new cross-linking route *via* the unusual collision kinematics of hyperthermal protons in unsaturated hydrocarbons: the case of poly(*trans*-isoprene)<sup>†</sup>

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The bombardment of a ~18 nm film of poly(*trans*-isoprene) molecules (~300 000 carbon atoms per molecule) with a mass-separated proton beam at 10 eV has been shown to induce highly efficient cross-linking of several macromolecules per incident proton. In this new method using physical means to conduct synthetic chemistry, the hyperthermal protons preferentially cleave C–H bonds because of their unusual kinematics in hydrocarbons, and the carbon radicals thus created initiate a polymerization chain reaction of the isoprene C=C bonds. The method produces ultrathin polymeric films *via* cross-linking with a dry process having high chemical selectivity and reactivity but requiring no thermal cost and no chemical additives, conditions that are commonly required in the fabrication of microelectronics and photonics.

The development of new means to cross-link molecules is constantly demanded by the market, for the production of novel materials and the improvement of current materials manufacturing in raising yields, reducing costs, and cutting chemical wastes. For example, new catalysts with improved cross-linking efficiency and chemical selectivity are invented,<sup>1</sup> new photoinitiators with higher quantum yields are introduced,<sup>2</sup> and new cross-linkers are designed and synthesized.<sup>3</sup> For those cross-linking applications in microelectronics, photonics and many other industrial sectors, the ideal strategy of synthetic chemistry should require no chemical additives, no catalyst, and no thermal curing.<sup>4</sup> In fact, many device fabrication reactions in these industries are dry processes with some of them assisted by energetic particles from a gas plasma. In polymer science and technology, the methodology of “cross-linking with activated species of inert gases” (CASING)<sup>5</sup> is an excellent example of this strategy. Recently, an intriguing cross-linking method<sup>6</sup> satisfying this strategy was developed by exploiting the unusual collision kinematics of a 10 eV proton with a hydrocarbon molecule in that the projectile proton can only transfer its kinetic energy effectively to the hydrogen atoms of the molecule and break the C–H bonds. In comparison, 10 eV protons

colliding with carbon and other chemical elements of the molecule do not have effective kinematic energy transfer and no physical bond cleavage is induced. As such, chemical selectivity and reactivity are accomplished by these proton collision kinematics. Although the validity of this concept has been confirmed both theoretically and experimentally, the effects of many reaction attributes have to be clarified and the exploitation of the method for specific synthetic applications will need to be explored.

In the present study, we elaborate on the reaction details of using hyperthermal<sup>6</sup> protons to initiate the polymerization of adsorbed poly(*trans*-isoprene), (–CH<sub>2</sub>CH=CCH<sub>3</sub>CH<sub>2</sub>–)<sub>n</sub> (PTI) for *n* ≈ 50 000. We choose to use the synthetic poly(*trans*-isoprene) as a model system because polyisoprene is an extremely versatile polymer precursor and is widely used in the synthesis of both traditional rubber products<sup>7</sup> and modern block copolymers.<sup>8</sup> For applications requiring polymeric thin films, the polyisoprene precursor can be dissolved in an organic solvent and deposited by spin-casting or other solution casting methods. Cross-linking the precursor film is expected to form an insoluble molecular layer with its mechanical properties dependent on the degree of cross-linking. Like the formation of copolymers, additional molecular species can be blended with the polyisoprene for the engineering of chemical properties in the cross-linked film.

In this work, poly(*trans*-isoprene) was spin-cast on a silicon wafer with a typical film thickness of 18 nm. The proton bombardment experiments were performed with a special mass separated low energy ion beam reactor<sup>9</sup> which delivered a proton beam at 10 eV with an energy spread of less than 0.6 eV to the sample in ultrahigh vacuum. The films before and after proton bombardment were characterized by *in situ* X-ray photoelectron spectroscopy (XPS) and *ex situ* atomic force microscopy (AFM). With XPS, a small change in film thickness can be deduced by changes of the relative intensities of C 1s and Si 2p signals, and the number of C=C bonds can be estimated by the intensity of the π–π\* characteristic energy loss structure<sup>10</sup> of the C 1s photoelectrons. Fig. 1a gives the XPS survey spectrum of the virgin PTI film which shows virtually nothing but carbon (C 1s) with weak signals of silicon which can still be detected with prolonged data acquisition. The film thickness measured by XPS is consistent with the nominal thickness of 18 nm. Prior to any proton bombardment, the film was soluble in a hexane rinse for 5 min, which is shown by the drastic reduction of the carbon signals and the surge of the silicon and its native oxide signals as shown in Fig. 1b. This dissolution treatment and the measurement of the insoluble film thickness have been adopted as a means to quantify the degree of cross-linking.

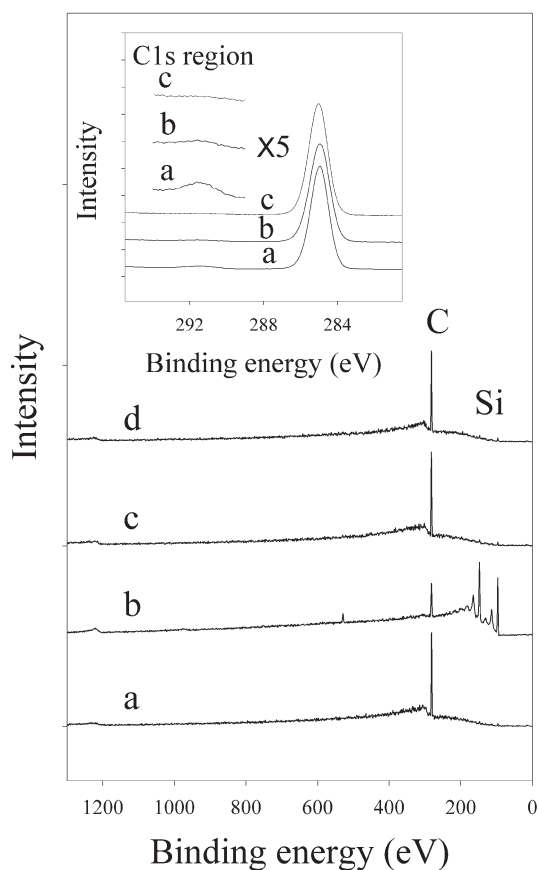
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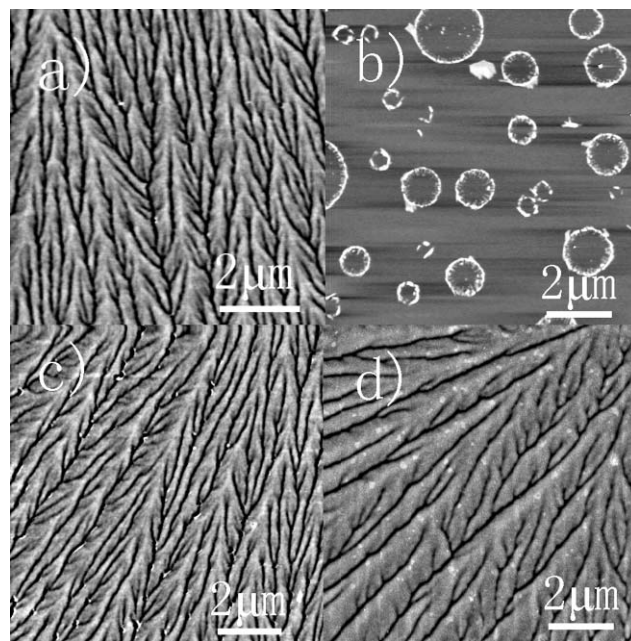
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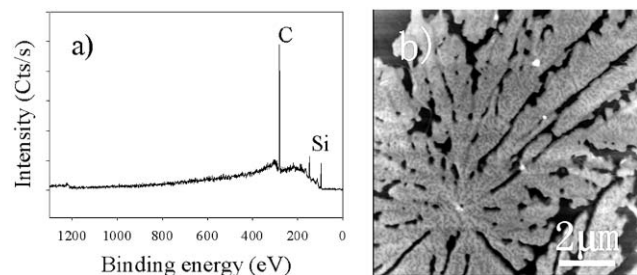
**Fig. 1** XPS survey spectra of PTI thin films: (a) virgin film; (b) virgin film after 5 min immersion in hexane; (c) 10 eV  $H^+$  bombarded film for a fluence of  $2 \times 10^{16} \text{ cm}^{-2}$ ; (d) the  $H^+$  bombarded film after 5 min immersion in hexane. Inset: XPS core level spectra of PTI films treated with different fluences of 10 eV  $H^+$  (a) zero, (b)  $2 \times 10^{16} \text{ cm}^{-2}$ ; and (c)  $5 \times 10^{16} \text{ cm}^{-2}$ .

For the films bombarded by a 10 eV proton beam to an ion fluence of  $2 \times 10^{16} \text{ cm}^{-2}$  ( $\sim 10$  atom-layer equivalents), no changes in both elemental composition (Fig. 1c) and film thickness are found except that the films are no longer soluble in hexane (Fig. 1d) no matter whether the solubility test is conducted with or without agitation by sonication. The film thickness results confirm that the hyperthermal proton bombardment causes neither any sputtering nor any material loss induced by C–C cleavage, and the change in solubility implies cross-linking. This interpretation is also supported by the AFM results on the virgin films and proton bombarded films before and after the dissolution test, as shown in Fig. 2. The AFM morphology images of the virgin and bombarded films show the interesting growth of dendritic features, which indicates a diffusion limited nucleation mechanism<sup>11</sup> during the spin-casting of the precursor film. The dendritic structure is not changed noticeably by the proton bombardment despite the observed evidence of cross-linking. The observed distension in Fig. 2d is attributed to the solvent swelling effect commonly observed in cross-linked polymers.<sup>12</sup> The virgin film is very smooth, with an average surface roughness (RMS) of 1.4 nm. The proton bombardment at 10 eV and a fluence of  $2 \times 10^{16} \text{ cm}^{-2}$  slightly increases the surface roughness to 1.9 nm and generates some particle-like features, which may be an effect of slight morphological restructuring due to random cross-linking.



**Fig. 2** AFM surface morphologies of PTI thin films: (a) virgin film, (b) virgin film after 5 min immersion in hexane, (c) 10 eV  $H^+$  bombarded film at a fluence of  $2 \times 10^{16} \text{ cm}^{-2}$ , (d)  $H^+$  treated film after 5 min immersion in hexane.

The above analysis shows, for the first time, the employment of hyperthermal protons as projectiles (initiators) to preferentially break C–H bonds of unsaturated linear polymer precursors and to initiate cross-linking polymerization. This is different from cross-linking saturated hydrocarbon molecules by hyperthermal proton bombardment because, for saturated hydrocarbon molecules, a sufficiently high fluence is required for the cleavage of a large number of C–H bonds before enough C–C cross-linked bonds can be formed to change the saturated hydrocarbon molecules in the virgin film to a stable and insoluble polymeric film.<sup>6</sup> For the unsaturated linear polymer precursors in this study, the main role of proton bombardment is to initiate the polymerization chain reaction. Indeed, the quantification of the degree of cross-linking by the retained thickness of the polyisoprene film surviving the dissolution test shows that a fluence of as little as  $1 \times 10^{14} \text{ cm}^{-2}$  is sufficient to induce a 90% retention of the poly(isoprene) film in the dissolution test (ESI<sup>†</sup>). From the fluence and the volume of the cross-linked polymer, we estimate that less than one proton projectile is required to change one poly(isoprene) precursor macromolecule from soluble to insoluble. With this low fluence, although the precursors are cross-linked to the extent of becoming insoluble in organic solvents, only some C=C bonds in the film are consumed and converted to cross-linked C–C bonds. The change in the number of residual C=C bonds in the proton bombarded film as a function of ion fluence can be measured semi-quantitatively by the intensity change of the  $\pi$ – $\pi^*$  characteristic energy loss structure of the C 1s photoelectrons.<sup>10</sup> At fluences below  $1 \times 10^{14} \text{ cm}^{-2}$ , the C=C consumption, *i.e.*, conversion of C=C to cross-linked C–C bonds, is effective because of the polymerization chain reaction. However, the subsequent C=C consumption requires more proton projectiles because the residual C=C bonds are well separated. The respective amounts of intensity reduction of the  $\pi$ – $\pi^*$  band are 47%, 87% and 97% for fluences of



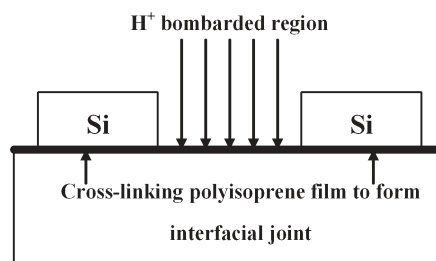
**Fig. 3** Characterization of the sample area about 2 mm away from the region bombarded by 10 eV  $H^+$ , with a hexane rinse to remove any insufficiently cross-linked PTI: (a) XPS survey spectrum, (b) AFM surface image.

$1 \times 10^{14}$ ,  $2 \times 10^{16}$ , and  $5 \times 10^{16} \text{ cm}^{-2}$ . Some of these results are included in the inset of Fig. 1. With these data, we estimate that about four 10 eV protons per isoprene ( $-\text{CH}_2\text{CH}=\text{CCH}_3\text{CH}_2-$ ) unit are required to consume all C=C bonds in the 18 nm film.

The difference between the cross-linking process in this study and the cross-linking polymerization of saturated hydrocarbon molecules is further illustrated by measurement of how far the cross-linking reaction can spread from the edge of a selected area receiving proton bombardment. This experiment is designed and conducted by using a shadow mask to define the proton bombarded area. Fig. 3 shows, with both XPS and AFM evidence, that for the poly(*trans*-isoprene) film, the effect of cross-linking is extended to 2 mm into the area with no proton bombardment even though the degree of cross-linking is lower than the area with direct proton bombardment. As expected, we do not observe this long-range polymerization chain reaction in the case of proton bombardment of saturated hydrocarbon molecules.

In addition to clarifying the science of using hyperthermal proton projectiles to initiate the chain reaction for cross-linking unsaturated linear polymer precursors, the results of this study also bear some hints on several potential industrial applications. The fact that an extremely low fluence is required to effectively cross-link the precursor film implies a high throughput and low bombardment side effects. We propose that this concept can be exploited for the development of an entrapping technology with the cross-linked carbon network to retain drug/protein molecules and with the diffusion/leakage properties adjusted by the degree of cross-linking. In fact, we have already confirmed the feasibility of this approach by the entrapment of poly(acrylic acid) molecules in a cross-linked polyisoprene film.

In addition, the spreading of the cross-linking reaction outside the line of sight of the proton beam can be exploited for the synthesis of tailor-made polymeric layers in enclosures such as microchannels or interfacial joints. This technique for modifying microchannel walls offers an alternative to the wet chemistry technology such as that recently disclosed by Honda *et al.*,<sup>13</sup> and for chemical molecular modification of microchannels in general.<sup>14</sup> The concept of fabricating a cross-linked polymer film in an



**Fig. 4** Schematic diagram showing the concept of cross-linking poly(*trans*-isoprene) in the shadowed area of the Si-Si interface for bonding the top silicon chips to the bottom silicon wafer.

enclosed area is demonstrated by the experiment illustrated in Fig. 4 in which the cross-linking of a poly(*trans*-isoprene) layer between two overlying silicon chips and a silicon wafer substrate is induced by proton bombardment of the exposed film area. The induced cross-linking in the enclosed interfaces is found to increase the mechanical strength of the interfacial poly(*trans*-isoprene) film between the two silicon work-pieces to the extent of keeping the overlying silicon chips chemically adhered to the bottom silicon wafer.

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