# *β*-Silyl Carbonyl Groups as New Photodegradation Units in Poly(butadienes)

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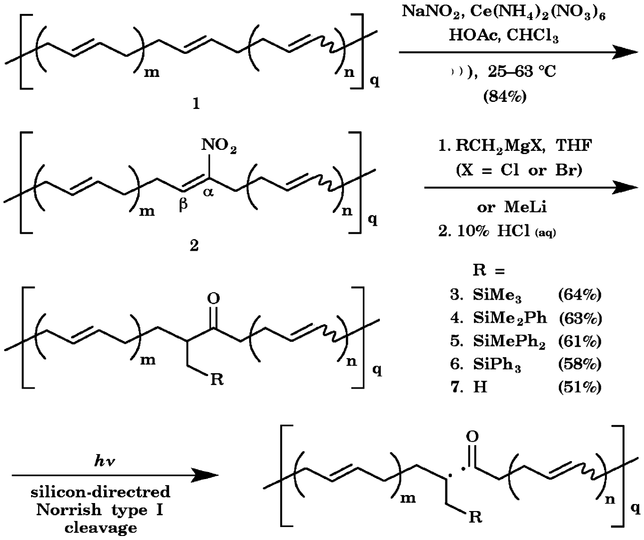
The invention of new methods for the production of photodegradable polymers[1] is at the high desire of modern industry and environmental protection.[2] We planned to apply the silicon-promoted Norrish type I cleavage in the development of new photodegradable polymers. Our design was based on a previous report that photolysis rates of ketones by UV light are increased by placement of a $Me_3Si$ group at the *β*-position.[3] Herein we disclose our new findings that incorporation of a *β*-(triorgano)silyl ketonic unit ($(-CH(CH_2SiR_3)C(=O)-)$) into poly(butadienes) allowed dramatic improvement on their photodegradability.

Poly(butadienes) **1** represent a broad class of diene rubbers, which play a prominent role in the industries of photolithography, microelectronics, and mechanical industry.[4] Several modified poly(butadiene) derivatives have been applied as positive-working photoresist compositions.[5] To incorporate *β*-silyl ketonic units in poly(butadienes) for increasing their photodegradability, we applied two reactions in sequence (see Scheme 1). First, we treated commercially available poly(butadienes) (**1**, 902 mg, $M_w$ 1.61 × $10^4$ and $M_n$ 1.51 × $10^4$) with sodium nitrite (2.30 g), ceric ammonium nitrate (3.66 g), and acetic acid (2.29 mL) in a sealed bottle under sonication at 600 W and 23−63 °C.[6] After 5.0 h, the desired nitroalkene-containing poly(butadienes) **2** were obtained in 84% yield upon neutralization of the reaction mixture with $Na_2CO_3$(s) and precipitation from hexanes. Polymers **2** exhibited IR absorptions at 1550 and 1346 $cm^{-1}$ resulting from the conjugated nitro group, a broad $^1H$ NMR signal around $\delta$ 7.03−7.24 ppm for the HC═CN proton, and two $^{13}C$ NMR signals at $\delta$ 151.07 and 136.32 ppm for the α and *β* carbons, respectively, in $HC_\beta{=}C_\alpha\text{-}NO_2$.[7]

Second, we incorporated the $Me_3SiCH_2-$ and the ketonic groups into **2** (159 mg) by using $Me_3SiCH_2MgCl$ (0.985 M in ether, 740 $\mu$L) in THF (10 mL) at 0 °C for 1.5 h. The resultant solution was acidified to pH ~2.0 with 10% aqueous HCl, and stirring was continued at room temperature for 7.0 h. After the silicon-promoted Nef reaction was complete,[8] we purified the precipitates with hexanes to give polymers **3** in 64% yield as a reddish-brown viscoelastomer. The presence of a carbonyl group in **3** is indicated by an IR absorption at 1724 $cm^{-1}$ and a $^{13}C$ NMR signal at $\delta$ 203.45 ppm. Furthermore, an IR absorption at 1250 $cm^{-1}$ and a broad $^1H$ NMR absorption around $\delta$ −0.21 to 0.17 ppm demonstrate the successful introduction of an $Si(CH_3)_3$ group.

**Scheme 1**



Various silyl groups may exhibit promoted effect in different degrees on the Norrish type I photocleavage and, thus, the photodegradability of new silyl ketone-containing polymers. Accordingly, we synthesized a series of silyl ketone-containing poly(butadienes) **4**−**6** in 58−63% yields by adding the corresponding silylmethyl Grignard reagents[9] ($R^1R^2R^3SiCH_2MgCl$; $R^1$, $R^2$, $R^3$ = Me or Ph) to poly(nitrobutadienes) **2** in THF at 0 °C (Scheme 1). The solutions were acidified to pH ~2.0 with 10% aqueous HCl at room temperature. Poly(nitrobutadienes) **2** exhibited IR absorptions at 1550 and 1346 $cm^{-1}$ for the conjugated nitro group. After a *β*-silyl ketonic unit was inserted to give silyl ketone-containing polymers **3**−**6**, an absorption showed up at ~1255 $cm^{-1}$ for Si−Me or at ~1115 $cm^{-1}$ for Si−Ph.[10]

To investigate photodegradation efficiency resulting from the *β*-(triorgano)silyl ketonic units in poly(butadienes), we carried out photolysis of several polymers in THF (0.26% w/v) at room temperature. A 450 W medium-pressure mercury UV lamp and a Pyrex filter ($\lambda \geq 300$ nm) were used to provide light with intensity 26.5 ± 0.8 $mW/cm^2$. The polymers included poly(butadienes) **1** as the reference, **3** ($M_w$ 1.74 × $10^4$ and $M_n$ 1.36 × $10^4$) with 4.4 mol % of the *β*-trimethylsilyl ketonic unit, **4** ($M_w$ 1.41 × $10^4$ and $M_n$ 1.06 × $10^4$) with 6.3 mol % of the *β*-(dimethylphenyl)silyl ketonic unit, **5** ($M_w$ 1.92 × $10^4$ and $M_n$ 1.43 × $10^4$) with 6.2 mol % of the *β*-(diphenylmethyl)silyl ketonic unit, and **6** ($M_w$ 1.48 × $10^4$ and $M_n$ 1.14 × $10^4$) with 9.0 mol % of the *β*-(triphenyl)silyl ketonic unit as well as polymers **7** ($M_w$ 1.47 × $10^4$ and $M_n$ 1.03 × $10^4$). Polymers **7**, containing 3.7 mol % of *β*-norsilyl ketonic unit, were prepared from **2** and MeLi (cf. $Me_3SiCH_2MgBr$ for **3**) by the same procedure for **2** → **3**.

We determined the average numbers of bond broken (i.e., $[(M_n)_0/M_n] - 1$) by GPC at different time intervals for polymers **1** and **3**−**7** (see Figure 1). Poly(butadienes) **1** were almost completely resistant to photolysis; in contrast, ketone-containing polymers **3**−**7** exhibited strong photodegradability. From the average numbers of bond broken and their degradable units, we obtained the ratios <1.0% for **1**, 20.3% for **3**, 14.9% for **4**, 17.1% for **5**, 13.7% for **6**, and 7.25% for **7** (see Table 1). These

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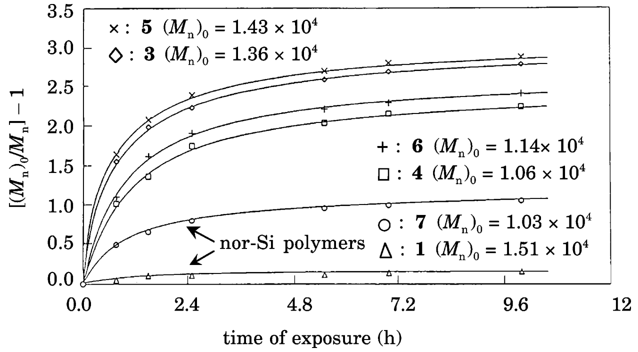

**Figure 1.** Average number of bond broken (i.e., $[(M_n)_0/M_n] - 1$) as a function of irradiation time by UV light with $\lambda \geq 300$ nm and intensity 26.5 ± 0.8 mW/cm$^2$ at room temperature.

**Table 1. Results of Photodegradation from $\beta$-(Triorgano)silyl Ketonic Units in Poly(butadienes) after Irradiation for 2.0 h**

| polymer | av no. of bond broken[a] | degradable unit[b] | efficiency (%)[c] |
|---|---|---|---|
| **3** | 2.07 | 10.2 | 20.3 |
| **4** | 1.55 | 10.4 | 14.9 |
| **5** | 2.22 | 13.0 | 17.1 |
| **6** | 1.75 | 12.8 | 13.7 |
| **7** | 0.642 | 8.85 | 7.25 |

[a] $[(M_n)_0/M_n] - 1$. [b] Calculated from $(M_n/M_m) \times$ (mol % of Si-containing unit). The term $M_m$ represents the average molecular weight of monomers. The mole percentage of Si-containing or methyl unit in polymers was determined by $^1$H NMR spectrometry. [c] Reflected by (the average number of bond broken)/(the degradable unit).

values indicate their efficiency of degradation. The strength of influence for a silyl group at the $\beta$ position of a carbonyl group follows the order $Me_3Si > MePh_2Si > Me_2PhSi > Ph_3Si > H$.

We found that the $\beta$-trimethylsilyl ketonic moiety displayed the most appealing photodegradation effect. Degradability was much higher for polymers **3** than the parent poly(butadienes) **1**. The effect is believed to come from the stabilization ability of a silyl group toward $\beta$ carboradical through "$\sigma$−$\pi$ hyperconjugation"[11] and, perhaps, "p−d homoconjugation".[12] Both the electronic and the steric effects resulting from the substituents on the silicon atom may affect its stabilization ability.[13] The net effect of a silyl group may come from the combination of both.

In conclusion, a new method was developed to make poly(butadienes) photodegradable and applicable as a positive photoresist. It involves incorporation of a $\beta$-(triorgano)silyl ketonic unit $[(-CH(CH_2SiR_3)C(=O)-]$ through nitration, Michael addition, and Nef reactions. The resultant poly[but-2-ene-*co*-3-(triorganosilyl) methylbutan-2-ones] possessed thermal stability and desired photodegradability. The outcomes will broaden the usage of polydiene rubbers.

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**Supporting Information Available:** Synthetic procedures and spectroscopic characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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