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Diacetylene-terminated diacetylene-containing polysiloxanes

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The presence of terminal diacetylenes in a diacetylene-containing poly(dimethylsiloxane) is demonstrated to emphasize their use as an alternative to other thermally reactive end groups for polymer cross-linking.

The preparation and thermal properties of linear siloxane–diacetylene polymers have been reported by Son and Keller.[1] These materials were synthesized by reacting dichlorosiloxanes with 1,4-dilithio-1,3-butadiyne (dilithiodiacetylene), which is generated by dechlorination of hexachlorobutadiene with *n*-butyllithium.[2] These polymers, with the repeat-unit structure shown in Fig. 1, can be referred to as diacetylene-containing poly(dimethylsiloxane)s (PDMS). As such, they belong to a large and growing group of polymers that contain diacetylene.[3–10] The diacetylene group has been incorporated into a variety of polymers for its latent reactivity, which depends on the primary structure of the host polymer, the concentration of the diacetylene groups, and the organization of the molecular environment in which the diacetylene groups are found. These same parameters govern the reaction temperature for thermally activated diacetylene groups. For example, increasing molecular order[11] or concentration[12] typically reduces the reaction temperature.

Many diacetylene-containing polymers are prepared by an oxidative coupling polymerization of α,ω-diethynyl-terminated monomers.[13–16] As a result, some chain-end ethynyl (*i.e.* terminal acetylene) groups may exist in the final structure. These functional groups also react thermally, but often at higher temperatures than the internal diacetylenes. Measured as an exotherm using differential scanning calorimetry (DSC), the peak reaction temperature for an ethynyl-terminated imide monomer is 300 °C, while the peak exotherm for the resulting diacetylene-containing polyimide is 250 °C.[17] Reactions of both functional groups have been employed as routes to cross-linked polymers.[18,19]

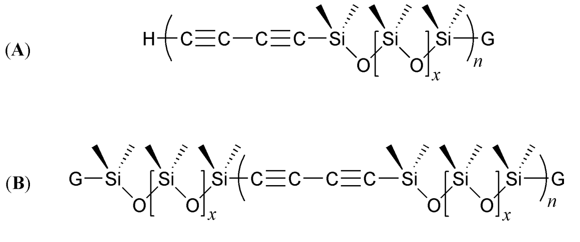

Fig. 1 Repeat-unit structure for (**A**) a diacetylene-terminated diacetylene-containing PDMS and (**B**) the corresponding polymer quenched with co-monomer, without terminal diacetylene groups. G represents an unspecified end group.[1]

For diacetylene-containing polymers prepared from dilithiodiacetylene,[2] such as the diacetylene-containing siloxanes,[1] primary diacetylene groups may be created at chain ends and are detectable when the molecular weight is limited.[20–22] Interestingly, and as opposed to terminal acetylenes, terminal diacetylenes react at temperatures below internal diacetylenes. Such groups can be avoided by quenching the polymerizations with the co-monomer, thus ensuring the presence of only internal diacetylenes.[23] However, for some applications, it may be desirable to thermally induce cross-linking at lower temperatures. Here, we demonstrate the presence of terminal diacetylenes in a diacetylene-containing poly(dimethylsiloxane) to emphasize their use as an alternative to other thermally reactive end groups for polymer cross-linking.

Synthesis of the diacetylene-siloxane polymers has been described previously.[1,24] For the work presented here, dilithiodiacetylene was reacted with 1,5-dichlorohexamethyltrisiloxane, so that $x = 1$ in Fig. 1. The procedure for preparation of the diacetylene-terminated diacetylene-containing PDMS [Fig. 1(**A**)] is as follows:† 10 mL THF and 9.75 mL *n*-butyllithium were transferred to a 50 mL Kjeldahl flask with a valved sidearm, containing a magnetic stir bar, and sealed with a rubber septum. The flask was then immersed in a dry ice–acetone bath contained in a low-form Dewar. While stirring, 0.95 mL (6.09 mmol) hexachloro-1,3-butadiene was added dropwise over 15 min. A deep purple color immediately formed, which darkened to a very dark black by the time all the hexachloro-1,3-butadiene had been added. The dry ice–acetone mixture was removed and the reaction mixture allowed to warm to room temperature with stirring. After 2 h at room temperature, the dry ice–acetone bath was replaced to cool the reaction mixture and 1,5-dichlorohexamethyltrisiloxane (1.66 mL, 6.09 mmol) was added dropwise. After this addition, the dry ice–acetone Dewar was removed and the reaction mixture allowed to warm to room temperature. A white solid formed in the reaction flask during this time. After 3 h at room temperature, the reaction mixture was poured into 30 mL saturated aqueous NH_4Cl solution at 0 °C. The reaction flask was then rinsed with diethyl ether into the NH_4Cl quench solution. The resulting two-phase mixture was transferred to a 250 mL separatory funnel and washed twice with distilled water (2 × *ca.* 50 ml). The dark organic phase was poured into an Erlenmeyer flask and dried over anhydrous Na_2SO_4. Filtration into a round-bottom flask was followed by rotary evaporation and then evacuation at room temperature for 5 h, to yield a slightly viscous dark brown liquid (1.3 g, 84% yield).

The diacetylene-containing PDMS without terminal diacetylene groups (**B**) was prepared by conducting the reaction on a larger scale (4 g theoretical yield), for a longer time (⩾8 h), and finally quenching the reaction with the dichlorosiloxane

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co-monomer. Following reaction at room temperature for about 10 h, the dichlorosiloxane co-monomer was added dropwise using a syringe. As each drop hit the surface of the reaction solution, it disappeared with a non-violent splash of white solid formation. Drops of dichlorosiloxane were added until this white solid formation subsided. The reaction was allowed to continue for another hour and then quenched in a saturated aqueous solution of NH_4Cl and worked up as before. The spectroscopic data showed peaks due to the internal diacetylenes, but lacked any peaks attributable to the terminal diacetylenes.

A selected portion of the infrared spectra of the diacetylene-containing PDMS (**B**) and the diacetylene-terminated form of the same polymer (**A**) is shown in Fig. 2. The absorption due to carbon–carbon triple bonds of internal diacetylenes appears at 2071 cm^{-1} for both polymers. The terminal diacetylenes give rise to the ≡C–H absorption at 3311 cm^{-1} and the two C≡C absorptions at 2192 and 2038 cm^{-1}; these peaks are completely absent from the spectrum of **B**. Other major peaks, including those due to C–H (2963 cm^{-1}), Si–O (1035–1085 cm^{-1}) and Si–CH_3 absorptions (800, 1261 cm^{-1}), appear in the IR spectra of both polymers.

DSC thermograms are shown in Fig. 3 for both polymers. The terminal diacetylene groups are thermally activated below 100 °C and exhibit a peak exotherm around 140 °C. The internal diacetylenes begin to react above 200 °C and exhibit a peak exotherm around 310 °C. The peaks are separated along the temperature axis. The thermogram of PDMS **B** does not exhibit a low-temperature exotherm, since no terminal diacetylenes are present. The DSC thermogram of PDMS **A** reveals an exothermic peak in Fig. 3 (solid line) for terminal diacetylene reaction that is twice the area of the exotherm due to internal diacetylene reaction. This polymer was annealed at 70 °C for 4 h. The resulting DSC thermogram still contained both exotherms, but the area under each was roughly equivalent. Another sample was annealed at 90 °C for 4 h and the area under the exotherm due to terminal diacetylenes was reduced to about 10% of the area in the unannealed sample. These annealing protocols caused negligible change in the area under the exotherm due to the internal diacetylenes. After annealing, the polymer became an insoluble solid. Thermogravimetric analysis of PDMS **A** revealed about 5% weight loss at 400 °C and a char yield of 57%. Polymer **B**, without terminal diacetylenes, exhibited char yields around 62%, which is similar to the value previously reported.[1]

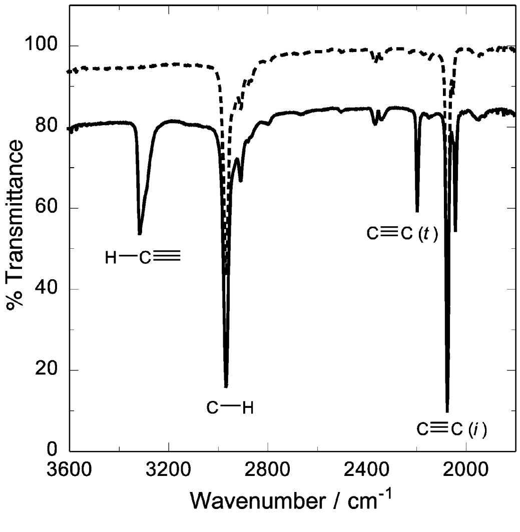

Fig. 2 Part of the infrared spectra of a diacetylene-containing PDMS (**B**; dashed line) and the diacetylene-terminated form of the same polymer (**A**; solid line). The terminal diacetylene C≡C bonds, signified by (*t*), give rise to bands at 2192 and 2038 cm^{-1}, while those of the internal diacetylenes, signified by (*i*), give a single absorption at 2071 cm^{-1}.

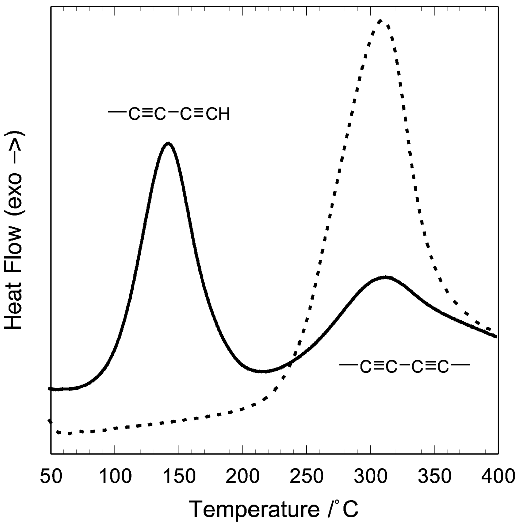

Fig. 3 DSC thermograms (10 °C min^{-1}) for a diacetylene-containing PDMS (**B**; dashed line) and the diacetylene-terminated form of the same polymer (**A**; solid line).

The terminal diacetylene groups shown here are easily observed because the molecular weight of the polymer is limited. Low molecular weights may be acceptable for materials to be used as thermosets. If high molecular weights are desired, then the molecular weight can be built up initially, followed by quenching with dilithiodiacetylene, as long as this dicarbanion does not cleave existing backbone bonds. An alternative route might be the use of $Me_3SiC{\equiv}CC{\equiv}CLi$, followed by catalytic cleavage of the trimethylsilyl groups to provide the terminal diacetylene groups.[25,26]

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Notes and references

†Glassware was baked at 120 °C for 24 h, then allowed to cool as dry argon passed through. All liquids were transferred with gas-tight syringes (Hamilton) pre-flushed 3 times with dry argon; needles were 20 gauge, 12 in stainless steel. Reagents were purchased from Aldrich unless noted otherwise. *n*-Butyllithium (2.5 M solution in hexanes) and tetrahydrofuran (anhydrous, 99.9%) were used as received. Hexachloro-1,3-butadiene (97%) was vacuum distilled (220 mT, 49.5 °C). 1,5-Dichlorohexamethyltrisiloxane (Gelest, 95%) was vacuum distilled over Mg turnings (400 mT, 31 °C). The latter two reagents were collected as clear liquids into round-bottom single-neck flasks with valved sidearms, stored under argon and sealed with rubber septa.

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