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Kinetic Studies of Photo-Cross-Linking of Acetylene-Containing Polyacrylates in the Presence of Tungsten Hexacarbonyl

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Introduction

Photolithography is an essential tool in the semiconductor and packaging industries for device fabrications that continues to meet the challenge of advanced chip technology and involves the use of positive or negative type photoresist materials.[1] With the advances in polymer chemistry and materials science, functional polymers have been developed to possess desirable properties for direct use in electronics[2] and photonics.[3] At present, the need for making better and smaller optoelectronic devices has generated an increasing interest in using photosensitive polymers as active materials in device fabrication without using photoresist materials. It would be desirable to develop a versatile polymer formulation from readily available polymers that can be transformed to become photosensitive.

We have recently demonstrated that the acetylene-containing polymers can be effectively cross-linked and patterned by UV irradiation if doped with a small amount of $W(CO)_6$.[4] Preliminary studies indicated photo-cross-linking of the acetylene-containing polymers proceeds in a mechanism similar to that of the metathesis polymerization of alkynes. However, the effects of some important parameters such as the acetylene content, amount of metal catalyst, and reaction time and temperature on this type of photo-cross-linking were still unknown. We report herein further spectroscopic and kinetic studies on the photo-cross-linking reactions of acetylene-containing polyacrylates **1a**−**e** in the presence of a small amount of $W(CO)_6$.

Experimental Section

The synthesis and characterization of acrylate polymers **1a**−**e** were reported previously.[4] The acetylene content in polymers **1a**−**e** ranges from 3 mol % (for **1a**) to 100 mol % (for **1e**). All the polymers could form thick films by solution casting on a substrate such as glass and KBr plate for spectroscopic studies.

Time-resolved FTIR experiments were carried out using a setup consisting of a Bomem Michelson 120 FTIR spectrometer, a custom-made heating unit and a light source for curing (see the setup drawing in the Supporting Information). The heating unit consists of a quartz tube and a heat conducting nickel coil to which a variable potential was applied in order to obtain the desired temperatures. UV curing of polymer films was done using an Ultracure 100SS Plus/Novacure system as a source with a 320−390 nm filter. The light guide is positioned at a distance of 12 cm away from the surface of the polymer film (see the setup drawing in the Supporting Information). The output dose at the sample surface is about 10 mW/cm^2 as measured using a radiometer. All the experiments were carried in a dark chamber, which had an argon inlet and outlet. The polymer films were cast on KBr plates, which were placed in a heating unit and irradiated while recording the IR spectra. IR spectra were collected every 5 s for the first 5 min and every 5 min for the following 55 min. The solid state ^{13}C CP/MAS NMR spectra were recorded using a Bruker AMX-300 spectrometer (300 MHz). The solution ^{13}C NMR spectra were recorded on a Bruker instrument at 100 MHz using tetramethylsilane as an internal reference.

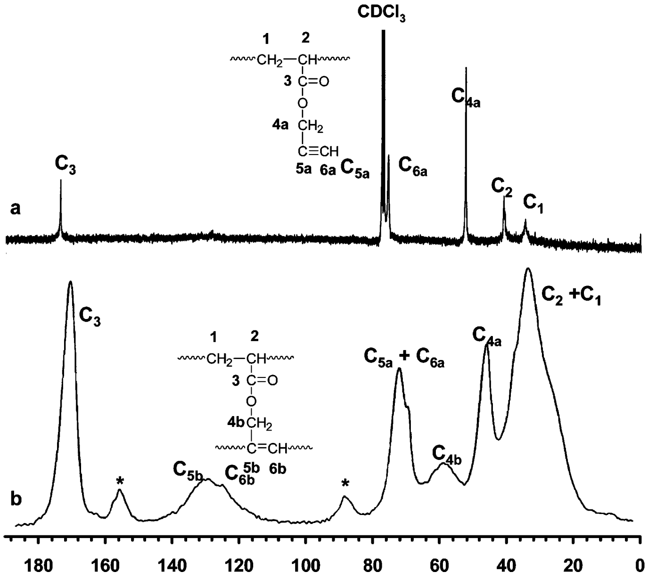

Figure 1. Changes in ^{13}C NMR spectra of polymer **1a**: (a) spectrum before irradiation taken in $CDCl_3$ and (b) ^{13}C CP/MAS NMR spectrum after UV irradiation for 60 min at 100 °C in nitrogen (∗ indicates a spinning sideband).

Results and Discussion

Preliminary IR studies indicated that the photo-cross-linking process of acetylene-containing acrylate polymers involves the formation of a series tungsten complex intermediates,[4] which were also identified in other photopolymerizations of acetylenes in the presence of $W(CO)_6$.[5] In this study, the structures of the cross-linked network were investigated using the solid state ^{13}C NMR spectroscopy. Polymer **1e** doped with 2 mol % (relative to the number of moles of the acetylene units) of $W(CO)_6$, which is equivalent to 0.78 wt % in polymer, was cast on a glass slide and cured for 60 min by light at 100 °C in nitrogen. Figure 1 displays the ^{13}C CP/MAS NMR spectra of the irradiated sample and the ^{13}C NMR of the nonirradiated sample of polymer **1e**.

As shown in Figure 1 (spectrum a), characteristic peaks of the nonirradiated sample were observed at 34 ppm (methylene, C_1), 40 ppm (methane, C_2), 52 ppm (methylene, C_{4a}), 75 ppm (acetylene, C_{6a}), and 79 ppm (acetylene, C_{5a}). For the cross-linked sample, four new peaks appeared (Figure 1, spectrum b) at 136 ppm (alkene, C_{5b}), 130 ppm (alkene, C_{6b}), and 65 ppm (methylene, C_{4b}), which indicated that the cross-linked structures contain a conjugated cis/trans C═C alkene moiety similar to the structure of polyacetylenes.

Factors Influencing the Photo-Cross-Linking. Knowing various factors that can affect the photo-cross-linking of this type of acetylene-containing polymers is important, to optimize the curing conditions and the quality of the photopatterns. The photo-cross-linking process of polymers **1a**−**e** was monitored using the time-resolved FTIR technique. The decrease in absorption of the ≡C−H stretch at 3300 cm^{-1} with the curing time

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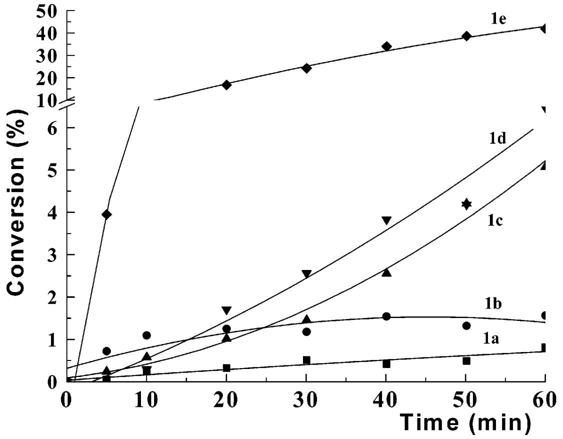

Figure 2. Conversion of polymers **1a**−**e** upon UV irradiation.

correlates to the conversion of the acetylene bonds due to mainly an intermolecular coupling reaction which leads to the polymer cross-linking (see the IR spectra in the Supporting Information). Although the intramolecular coupling of the two acetylene units could not be ruled out, it is unlikely to occur to a large extent and will not lead to polymer cross-linking. Thus, the degree of conversion (x) of the acetylene groups in the polymers can be calculated according to eq 1, from the ratio of the absorbance at time t during the curing reaction to the absorbance before curing ($t = 0$).

$$x = 1 - \frac{(A_{\equiv \mathrm{CH}}/A_{\mathrm{esterC{=}O}})_t}{(A_{\equiv \mathrm{CH}}/A_{\mathrm{esterC{=}O}})_{t=0}} \qquad (1)$$

Considering a variation in thickness of the polymer films, the absorption of the carbonyl bond of the ester moiety in the polymers is used as an internal reference, as the ester group does not involve in the photo-cross-linking reaction. Therefore, the integrated value of the acetylene ≡C−H absorption peak at 3300 cm^{-1} was normalized to the absorption peak of the ester C═O at 1730 cm^{-1}. The degree of photo-cross-linking can be related to the degree of conversion of the acetylene units (x), under the assumption that there is no intramolecular coupling of the acetylene units during the photo-cross-linking process.

Effect of the Acetylene Content. Polymer films doped with 0.1 mol of W(CO)$_6$ per mole of the acetylene unit were cast on KBr plates and exposed to 320−390 nm UV light at room temperature in argon for 1 h. The degrees of conversion for polymers **1a** and **1b** were only 0.8% and 1.5%, respectively, after 60 min of irradiation (Figure 2). Such a low conversion rate can be attributed to the low content of the acetylene groups in the polymers **1a** (2.9 mol %) and **1b** (11.6 mol %). This can be easily understood by the fact that the low content of the acetylene group in the polymers means a smaller number of the reactive sites in close vicinity and less opportunity for any intermolecular (and intramolecular) coupling. With a higher content of the acetylene moieties incorporated into the polymers, the conversion rate increased to 5% for polymer **1c** with 34.5 mol % of acetylene content and to 42% for **1e** with 100 mol % of acetylene. In general, for these acetylene-containing polymers about 5% conversion or 10% cross-linking is enough to cause the polymer become insoluble and allow for the image development.

Effect of the Amount of W(CO)$_6$. Since polymer **1c** containing a sufficient number of cross-linkable acetylene units was able to achieve a significant change in IR, it was used in subsequent studies on the effect of the amount of W(CO)$_6$ and the curing temperature. Thin films of polymer **1c** doped with different amounts of W(CO)$_6$ (1, 2, 5, 10, and 20 mol % per mole of the acetylene unit) were irradiated at 320−390 nm for 1 h at room temperature in argon. Figure 3 show the degree of conversion or extent of photo-cross-linking vs the amount of W(CO)$_6$ for different irradiation time. The acetylene conversion was highest when 10 mol % of W(CO)$_6$ was used and reached a maximum of 17.7% after curing for 60 min. It is interesting to note that with 20 mol % of W(CO)$_6$ the degree of the acetylene conversion actually decreased, implying that a larger amount of W(CO)$_6$ would lead to the formation of the photopatterns in poor quality (e.g., poor contrast) due to relatively less cross-linking. According to the proposed mechanism,[5] in the presence of a large amount of W(CO)$_6$ there will be less acetylene available for subsequent coupling or cross-linking reaction.

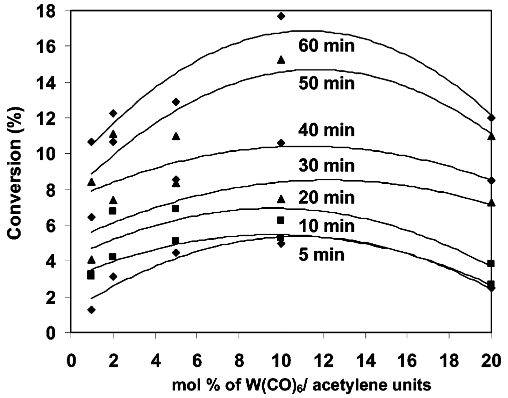

Figure 3. Conversion of the acetylene moieties in **1c** containing different amounts of W(CO)$_6$ at different irradiation time.

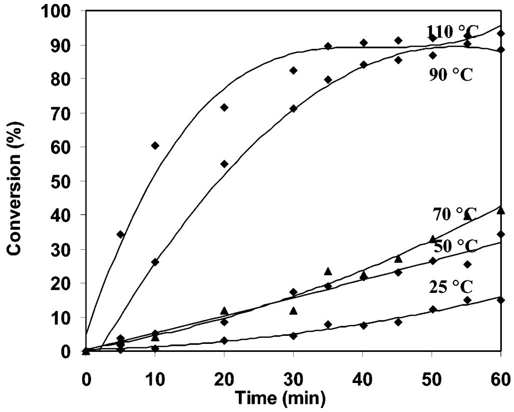

Figure 4. Conversion vs time at different curing temperatures for polymer **1c**.

Effect of the Curing Temperature. Photo-cross-linking of films of polymer **1c** doped with 10 mol % of W(CO)$_6$ was carried out at five different temperatures in argon. Figure 4 displays the degree of conversion of the acetylene units vs time at 25, 50, 70, 90, and 110 °C. The conversion rate increased with an increase in the reaction temperatures. At temperatures below the glass transition temperature (T_g) of polymer **1c** (51 °C), a relatively slow conversion rate was observed (e.g., 34% at 50 °C). With increase of polymer chain mobility at temperatures above T_g, the conversion rate significantly increased, reaching up to 90% within 35 min at 110 °C. A failure to reach 100% conversion even after additional

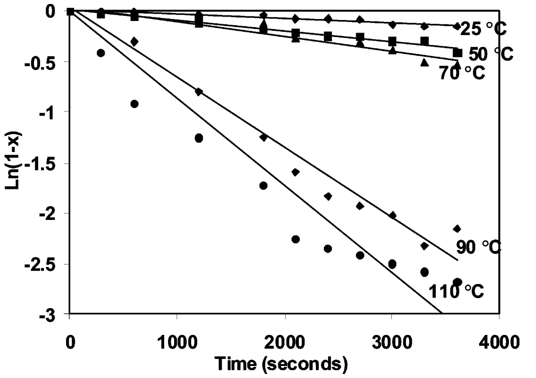

Figure 5. Kinetic plot of ln(1−*x*) vs time for polymer **1c**.

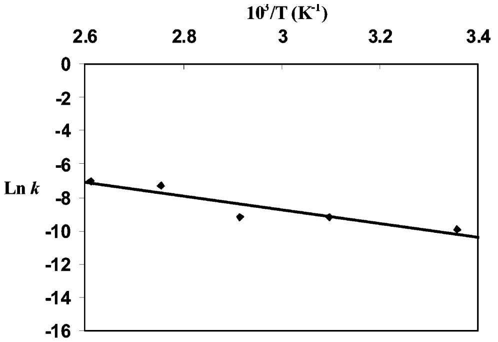

Figure 6. Arrhenius plot of the photo-cross-linking reaction of polymer **1c**.

Table 1. Kinetic Data of the Photocross-linking Reaction of Polymer 1c

temp (°C)	rate const $k \times 10^3$ (s^{-1})	regression coeff (R^2)
25	0.05	0.9254
50	0.1	0.9664
70	0.1	0.9359
90	0.7	0.9720
110	0.9	0.9093

photocuring for 25 min could be explained by a topological limit for the remaining acetylene groups in the cross-linked network and lowered chain mobility due to the formation of the cross-linked network.[6] It should be noted that at 110 °C these acetylene-containing polymers do not undergo thermal cross-linking reactions, in absence of UV light.[4] Furthermore, regarding the photopattern formation, at the temperature of 20 °C above the polymer's T_g, no decrease in the pattern resolution was observed. However, at the temperatures of 40−50 °C above the T_g, the polymer films began softening and gluing onto the surface of the contact mask.

Kinetic Study. Plots of ln(1−*x*) vs time, where *x* is the degree of conversion of the acetylene moieties in polymer **1c**, show that the photo-cross-linking reaction follows first-order kinetics (Figure 5). Linear regression analysis using the least-squares method was used to fit the data. The kinetic rate constants, *k*, derived from the slopes of each reaction isotherm, are listed in Table 1.

From the Arrhenius plot, ln *k* vs 1/*T*, where *T* is the reaction temperature, the activation energy of this type of photo-cross-linking reaction was determined (Figure 6). The activation energy was calculated to be 34.1 kJ/mol for photo-cross-linking of polymer **1c**, indicating the photo-cross-linking rate is temperature dependent. The linearity of the data plot as determined from the regression coefficient (R^2) is 0.8512, due to experimental errors. By excluding the data point corresponding to the experiment run at 70 °C, the R^2 value improved to 0.9738.

A similar kinetic study was carried out on polymer **1b**. It was found that 93% of the acetylene moieties were converted or reacted after photocuring at 100 °C and the activation energy for photo-cross-linking of polymer **1b** was 17.7 kJ/mol. In comparison with polymer **1c**, the activation energy clearly depends on the T_g of the polymer and is lower for the polymer with a lower T_g or higher chain mobility.

The photo-cross-linking of polymers **1a**−**c** in the presence of $W(CO)_6$ should involve at least two distinct steps: (1) formation of a vinylidene derivative [$-CH_2-CH{=}C{=}W(CO)_5$] and (2) dimerization of the complex or addition to the free acetylene unit. The first step is a known photolytic process, as shown by Marshall et al.[5a] and the subsequent dimerization or addition is also known in the acetylene polymerization. Our kinetic studies suggest that for the given polymer system the formation of the tungsten−acetylene complex is the overall rate-determining step and the subsequent reaction of reactive intermediates proceed relatively much faster. As a result, both the acetylene and $W(CO)_6$ content in the polymer are the main factors that influence this photo-cross-linking process.

Conclusions

The formation of polyene-type structures from photo-cross-linking of acrylate polymers containing the pendent acetylene groups in the presence of $W(CO)_6$ was confirmed by ^{13}C CP/MAS NMR studies. The first-order kinetics with activation energies of 34.1 and 17.7 kJ/mol were found for polymers **1b** and **1c**, respectively. The overall reaction rate is governed by the amounts of the acetylene groups and tungsten catalyst present in the polymer. The results obtained from this study are useful to design a suitable polymer formulation as photosensitive materials for making photopatterns.

Supporting Information Available: Schematic representation of the setup for time-resolved FTIR experiments and FTIR spectra of polymer **1d** at different stages of photo-cross-linking. This information is available free of charge via the Internet at http://pubs.acs.org.

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