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Metal catalyzed photocrosslinking of polymers containing pendant propargyl groups

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Abstract

Polymers containing the pendant propargyl groups can be effectively crosslinked upon UV irradiation in the presence of a small amount of $W(CO)_6$. The alkyne–tungsten carbonyl complex was formed initially as evident by IR spectroscopy, which was involved in the subsequent crosslinking reaction. Analyses by UV, IR, and ^{13}C NMR CP/MAS spectroscopic methods confirmed the polymer crosslinking as a result of the conversion of the acetylenic units to the polyene and diacetylene moieties in the crosslinked system.

Keywords: Photocrosslinking; Polymers containing propargyl groups; Tungsten hexacarbonyl

1. Introduction

The alkynyl groups in the polymer main-chain or side-chain can induce a crosslinking reaction by heating [1–4], radiation [5–7], gamma-irradiation [8] and plasma treatment [9,10]. Diacetylene monomers are known to be photochemically polymerized [11] and a variety of polymers containing the diacetylene moiety in the main-chain can be crosslinked by UV light [12]. However, the polymers having the pendant 2-propynyl (or propargyl) groups are not readily crosslinkable by UV irradiation, primarily due to low reactivity of the alkylethynyl group towards conventional radical and ionic catalysts [13,14].

On the other hand, it is known that the polymerization of mono-substituted acetylenes can be initiated by photolysis of the Ziegler–Natta catalysts such as $Ti(O\text{-}n\text{-}Bu)_4 \cdot 4Et_3Al$ [15] and $Fe(acac)_3 \cdot 3Et_3Al$ [16], and other metal (Co, Ni, Rh) catalysts [17]. Oligomerization and polymerization of substituted acetylenes also proceed upon photolysis in the presence of transition metal (Cr, Mo, W) carbene complexes [18,19] or their binuclear complexes [20]. Recent investigations indicate that the use of a pre-formed carbene complex is not necessary since active species for alkyne polymerization can be formed by photolysis of $M(CO)_6$ ($M = W$, Mo) with terminal alkynes [21–25]. The presence of halogenated solvents [26,27] or Lewis acids [28] also affect the alkyne polymerization in this system. The key step in the catalyst generation involves the photochemical reaction of $W(CO)_6$ with terminal alkynes leading to the formation of $[(\eta^2RC{\equiv}CH)W(CO)_5]$ intermediate and the subsequent vinylidene intermediate of $[R(H)C{=}C{=}W(CO)_5]$ via a rearrangement [21,29].

Based on the chemistry of metal-catalyzed photopolymerization of mono-substituted acetylenes, it is conceivable to develop a new metal-catalyzed photocrosslinking polymer system. To demonstrate this feasibility, we report herein the first example of the $W(CO)_6$-catalyzed photocrosslinking of polymers containing the pendant propargyl group.

2. Experimental

2.1. Synthesis

Poly(ethylene-*alt*-maleic anhydride), $M_w = 100{,}000$–$500{,}000$, was purchased from Sigma-Aldrich Canada Ltd. and had a glass transition temperature of 150 °C after being dried in a vacuum oven (5 mmHg) at 100 °C overnight prior to use. Aniline, propargylamine hydrochloride and other reagents were used as received from

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Sigma-Aldrich. *N*,*N*-Dimethylacetamide (DMAc) was dried over calcium hydride and vacuum distilled.

A typical synthesis is given for polymer **3**: a mixture of poly(ethylene-*alt*-maleic anhydride) (1.26 g, 10.0 mmol), propargylamine (0.28 g, 5.00 mmol), aniline (0.47 g, 5.00 mmol) and DMAc (20 ml) was heated to 40 °C under nitrogen for 6 h. After cooling to room temperature, 1.5 ml of acetic anhydride and 1 ml of triethylamine were added. After stirring for 5 h at room temperature, the reaction mixture was poured into methanol (100 ml). The precipitated solid was collected by filtration, washed with methanol and dried in oven at 50 °C under vacuum (5 mmHg) to give 1.31 g (72% yield) of white powders. IR (KBr, cm^{-1}): 3276 (≡C–H), 2123 (C≡C), 1707, 1669 (–C=O, imide); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.43, 7.24 (s, –CH, aromatic), 4.10 (s, –CH$_2$, propargyl), 3.12 (m, ≡C–H), 2.77–2.67 (m, –CH, backbone), 2.1–1.5 (m, –CH$_2$, backbone).

2.2. Measurement

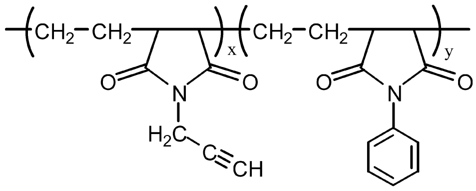
^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or Bruker-400 spectrometer. The solid-state ^{13}C MAS/CP NMR spectra were recorded on Bruker ASX-200 spectrometer. The chemical shifts relative to tetramethylsilane as internal reference are reported in the ppm scale. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrophotometer. Solubility tests were carried out by dissolving about 10 mg of polymer in 1 ml of studied solvent. Glass transition temperatures (T_gs) were determined on a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 20 °C/min in nitrogen. The onset temperature for 5% weight loss were determined using a Seiko 120 thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen. Absorption spectra were recorded on a Perkin Elmer Lambda 900 UV–Vis-NIR spectrophotometer. The thickness and refractive index of the film sample were measured at 1550 nm using the Metricon's prism coupling instrument.

3. Results and discussion

3.1. Polymer synthesis and characterization

Polymers containing the propargyl groups (**1–4**) and the phenyl group (**5**, Table 1) were synthesized by grafting poly(ethylene-*alt*-maleic anhydride) with propargylamine and aniline. The acetylene content in copolymers **2–4** was determined by ^{1}H NMR spectroscopy, which could be easily controlled by adjusting the ratio of propargylamine and aniline during the grafting reaction. The composition and ratio of the pendant groups also affect the thermal and physical properties of these polymers. The glass transition temperatures (T_g) of polymers **1–5** were in the range 123–163 °C, close to that (150 °C) of the parent polymer and correlate linearly to the amount of the acetylene units (Fig. 1). For polymers **1–4**, a broad exothermic peak due to thermal crosslinking of the acetylene groups was observed in a range from 200 to 350 °C. Similarly, with an increase of the acetylene content the refractive indices of the polymers decreased linearly, going from the refractive index of 1.5642 at 1550 nm for polymer **5** with no acetylene units to 1.5239 for polymer **1** containing 100% acetylene units (Fig. 1). Both T_g and index data clearly support the nature of random copolymers **2–4**. The onset temperature (T_d) for 5% weight loss in nitrogen for polymers **1–5**, as assessed by thermogravimetry, was above 400 °C, indicating a good thermal stability of this type of maleimide polymers. The observed increase in T_d related to an increase in the aliphatic propargyl content in these polymers was mainly due to the fact that thermal crosslinking of the acetylene groups in polymers **1–4** improved their thermal stability.

Table 1
Characterizations of polymers **1–5**



Polymer	Composition *x*/*y* (mol)[a]	T_g (°C)[b]	T_d (°C)[c]	Refractive index[d]
1	100/0	124	434	1.5239
2	72/28	138	416	1.5409
3	50/50	147	405	1.5467
4	25/75	157	399	1.5547
5	0/100	163	407	1.5642

[a] Relative ratio calculated from ^{1}H NMR data.

[b] Taken from the second scans after quenching from 185 °C by DSC at the heating rate of 10 °C/min.

[c] Onset temperature for 5 % weight loss in nitrogen, as assessed by thermogravimetry at the heating rate of 10 °C/min.

[d] Measured at the wavelength of 1550 nm.

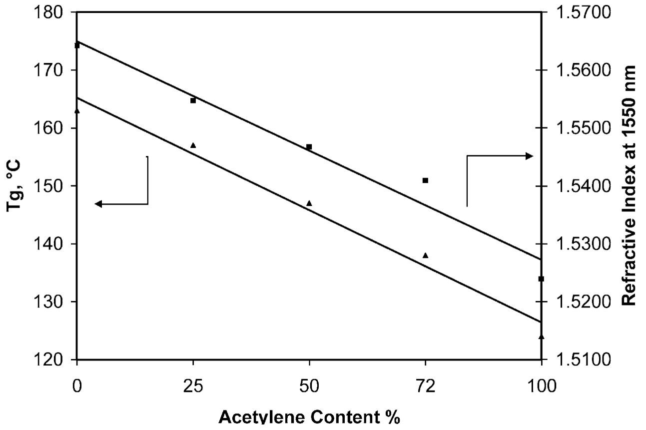


Fig. 1. Correlation of the glass transition temperatures (▲) and refractive indices (■) to the acetylene content in polymers **1–5**.

3.2. Polymer photocrosslinking

Photocrosslinking of polymers **1–4** in the presence of a small amount of $W(CO)_6$ was demonstrated in solution and the films. UV irradiation (320–390 or 250–450 nm) was carried out at ambient temperatures using a Novacure spot-cure light source. The solutions of polymers **1–4** in 1,1,2,2-tetrachloroethane (TCE) doped with 2 wt% of $W(CO)_6$ became gel after UV irradiation (100 mW/cm^2) for 20 min. On the contrary, the polymer solution without the tungsten catalyst remained fluid under the same irradiation conditions. Thin films (2–3 μm in thickness) of polymers **1–4** containing 2 wt% of $W(CO)_6$, cast from a 10% polymer solution on a silicon wafer, could not be dissolved or swelled in TCE after UV irradiation for 20 min. A fine pattern could be obtained after irradiation through a contact mask and developing with TCE. In comparison, the irradiated films without $W(CO)_6$ could still be dissolved or swelled in TCE.

The photocrosslinking process for polymers **1–4** can be readily monitored by IR spectroscopy. Polymer **1** with 2 wt% of $W(CO)_6$ displayed a characteristic band at 2132 cm^{-1} due to C≡C stretching vibration (Fig. 2(A), spectrum a), which disappeared after UV irradiation for 40 min (Fig. 2(A), spectrum d). Meanwhile, the relative intensity of peaks for ≡C–H at 3279 and ≡C–C at 973 cm^{-1} decreased significantly as a result of the crosslinking reaction of the acetylene units. In comparison, for polymer **1** without $W(CO)_6$, the peaks at 2132, 3279 and 973 cm^{-1} only decreased slightly after UV irradiation for 40 min (Fig. 2(C), spectrum d). Therefore, $W(CO)_6$ is necessary for the photochemical crosslinking of polymers having the pendant propargyl groups. In order to investigate the critical role that $W(CO)_6$ plays in polymer photocrosslinking, changes in the CO bands were monitored by IR during the initial stage of irradiation of the film of polymer **1** doped with 20 wt% of $W(CO)_6$. After 30 s of irradiation, the small shoulder peak at 2016 cm^{-1} and large peak at 1973 cm^{-1} characteristic for $W(CO)_6$ (Fig. 2(B), spectrum a) almost disappeared. At the same time, new peaks at 1965 and 1920 cm^{-1} were shown (Fig. 2(B), spectrum b), suggesting the dissociation of $W(CO)_6$ and the formation of the (η^2-alkyne)tungsten pentacarbonyl complex [30]. The positions of these two new bands are in agreement with the reported values for (η^2RC≡CH)$W(CO)_5$ [21]. Further irradiation resulted in a complete disappearance of the carbonyl peaks (Fig. 2(B), spectrum c), as in the case for (η^2RC≡CH)$W(CO)_5$ [21,29], presumably leading to the formation of various active tungsten complexes that are responsible for subsequent photochemical reaction of the acetylene units in polymers. It was also found that it is necessary to continue the UV irradiation even after $W(CO)_6$ is completely consumed.

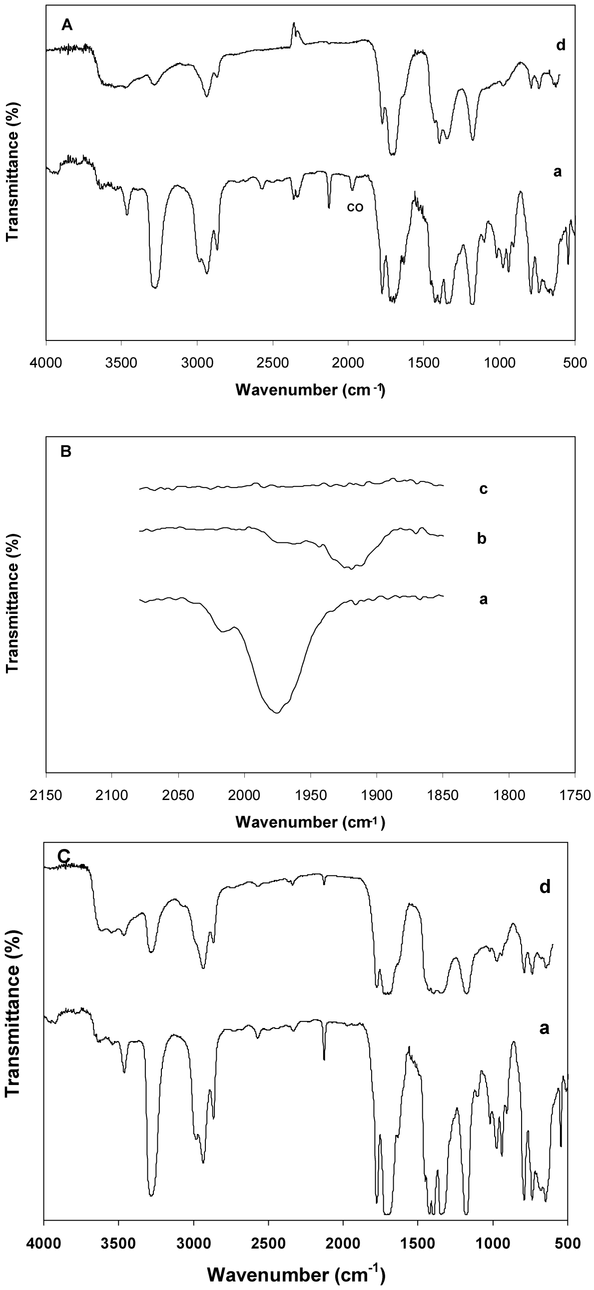


Fig. 2. IR spectra of the films of polymer **1** (A) doped with 2 wt% of $W(CO)_6$, (B) doped with 20 wt% of $W(CO)_6$, and (C) without $W(CO)_6$. UV irradiation time for each of labeled spectra: a (0 s or before irradiation), b (30 s), c (5 min) and d (40 min).

To elucidate the structural features of the crosslinked polymers, the UV spectra of polymer **4** doped with 2 wt% of $W(CO)_6$ were taken before and after UV irradiation. Polymer **4** itself has no significant absorption above 300 nm (Fig. 3, spectrum a). After irradiation at 320–390 nm for 40 min, a significant increase in the absorption intensity at about 225 nm could be seen (Fig. 3, spectrum b), which are characteristics for the diene functionality [31]. After being irradiated at a broader range of 250–450 nm for 40 min, a strong, broad absorption was observed in the region of 200–450 nm (Fig. 3, spectrum c), which are ascribed to the presence of the diene, triene, and even polyene units [31].

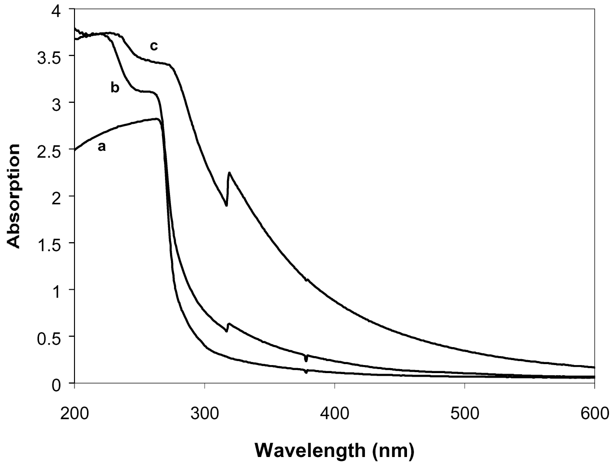


Fig. 3. UV–Vis spectra of polymer **4** doped with 2 wt% of $W(CO)_6$ obtained (a) before UV irradiation, (b) after irradiation at 320–390 nm for 40 min, and (c) after irradiation at 250–450 nm for 40 min.

Further investigation by the solid-state ^{13}C MAS/CP NMR spectroscopy indicated the involvement of the acetylene units in polymer photocrosslinking. After UV irradiation of polymer **1** containing 3 wt% of $W(CO)_6$ for 40 min, the peak intensities for the two acetylene carbons (≡C– at 78.2 ppm and ≡CH at 73.3 ppm) decreased (Fig. 4, spectrum b), relative to those before UV irradiation (Fig. 4, spectrum a). Meanwhile, a new broad peak appeared at around 130 ppm, corresponding to the C=C carbons. In addition, a new peak was observed at 75.3 ppm for the crosslinked sample (Fig. 4, spectrum b), due to the diacetylene moiety formed from the self-coupling reaction of the acetylene units [32]. No other significant changes were observed in the NMR spectrum of the irradiated sample. Thus, the crosslinking process only involves the photochemical reaction of the propargyl units, rather than other groups such as the imide units [33], as a result of the formation of the polyene and diacetylene moieties.

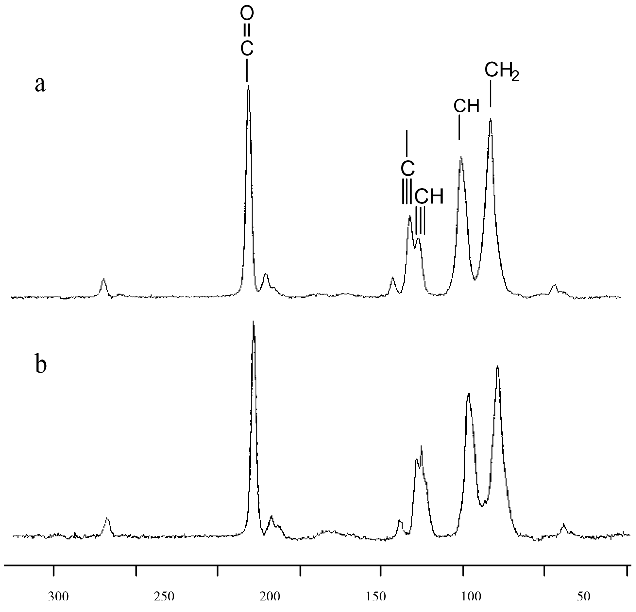


Fig. 4. ^{13}C CP/MAS NMR spectra of polymer **1** obtained (a) before UV irradiation and (b) after doping with 2 wt% of $W(CO)_6$ and UV irradiation for 40 min.

4. Conclusion

This work has demonstrated a new class of photocrosslinkable polymers that can have various types of the repeat units containing the pendant propargyl group. The use of a small amount of $W(CO)_6$ or other metal catalysts is essential for effective photocrosslinking. These photocrosslinkable polymers are potentially useful as a host for functional molecules (e.g., nonlinear optical chromophores) and as optical waveguide materials as their refractive indices could be tailored at the telecommunication wavelengths (e.g. 1550 nm).

Acknowledgements

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