

# Reversible Photoreaction of C<sub>60</sub>-Containing Poly(vinyl alcohol)

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Received 14 August 1997; accepted 22 January 1998

**ABSTRACT:** Poly(vinyl alcohol) (PVA) was reacted with strong base NaH to convert its pendant hydroxy to oxy anions, followed with nucleophilic addition to buckminsterfullerene-C<sub>60</sub>. The resulted PVA(C<sub>60</sub><sup>-</sup>Na<sup>+</sup>)<sub>n</sub> products were then converted to PVA(C<sub>60</sub>H)<sub>n</sub> by stirring with a strong acid cation exchanger of the H<sup>+</sup> form. The reduced viscosities of PVA(C<sub>60</sub>H)<sub>n</sub> decreases with amount of C<sub>60</sub>, and are between 0.38 and 0.66 dL/g compared to 1.97 dL/g of the original PVA. Repeated photocrosslinking under 300 nm light and photocleavage under 254 nm light of these C<sub>60</sub>-containing PVAs were investigated in DMSO by tracing their UV absorption variations at 325 nm (maximum absorption of C<sub>60</sub>H). It is confirmed that both PVA(C<sub>60</sub>H)<sub>n</sub> exhibit excellent reversibility at least under the observed three cycles. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 605–611, 1998

**Key words:** buckminsterfullerene-C<sub>60</sub>; poly(vinyl alcohol); reversible photoreaction

## INTRODUCTION

Since the development of methods for mass production of buckminsterfullerenes, there has been great interest in fullerene-containing polymers.<sup>1–20</sup> The fullerene-containing polymers can be roughly divided into two categories. One category consists of polymers of covalently linked fullerenes,<sup>6–11</sup> and the other includes copolymers in which fullerenes are part of the polymer structure.<sup>12–20</sup> For styrene-based copolymers, there was a brief article on the preparation of a highly crosslinked fullerenated polystyrene using a Friedel-Crafts type reaction.<sup>18</sup>

Thymine bases with long alkyl chain convert to photodimers upon irradiation with UV light near

the  $\lambda_{\max} = 288$  nm, which is known to have a lethal effect in biological systems.<sup>21</sup> However, the photodimerization is a reversible reaction and the photodimers are cleaved to starting thymines efficiently upon irradiation at 240 nm. This reversible and thermally stable photochromic system of thymine has been applied to reversible photorecording system.<sup>22,23</sup> The polymers containing thymine bases have high resolution and high sensitivity when used as negative, positive, and chemical amplification photoresists for microlithography.<sup>24–27</sup> We have synthesized coumarins with long alkyl chain by condensation of umbelliferone with alkanoyl chlorides, and their reversible [2 + 2] photocyclodimerization (formation of cyclobutane) behaviors have been investigated in detail after dispersing in poly(vinyl acetate).<sup>28</sup> Reversible photoreactions of polymers containing coumarin chromophores in the pendant group or in the main chain have also been investigated.<sup>29–35</sup> Fischer mentioned that a C<sub>60</sub> cage can be linked as a strain of pearls through formation of cyclobutane via [2 + 2] cyclodimerization.<sup>4</sup>

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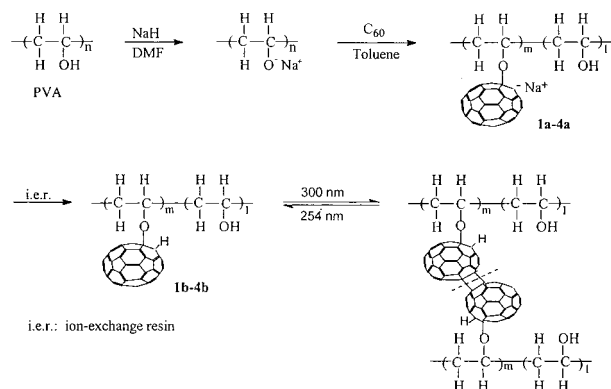
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Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC 85-2216-E-006-050

*Journal of Applied Polymer Science*, Vol. 70, 605–611 (1998)

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CCC 0021-8995/98/030605-07



Scheme 1

The objectives of this work is mainly to demonstrate the reversible photocrosslinking (300 nm) and photocleavage (254 nm) properties of  $C_{60}$ -containing PVA in dimethyl sulfoxide (DMSO).

## EXPERIMENTAL

### Materials

Buckminsterfullerene  $C_{60}$  was from Hoechst AG, with a purity higher than 99.4% (gold grade) and used as received. Poly(vinyl alcohol) was purchased from Merck with a molecular weight of 72,000 and used without further purification. Sodium hydride (NaH: 60% in oil) was from Wako Chemical Co. Ion exchanger Amberlite® IR-120 was from Merck, and it was a strong acid cation exchanger of the  $H^+$  form with a particle size between 0.3 and 1.2 mm. Other chemicals and solvents were pure reagents and LC grade reagents, respectively, and purified by the conventional methods before use.

### Synthesis of $C_{60}$ -Containing PVA (Scheme 1)

To a 50-mL two-necked glass reactor was added 0.122 g PVA (OH group =  $2.77 \times 10^{-3}$  mol) and 20 mL *N,N*-dimethylformamide (DMF). The mixture was then heated to  $80^\circ\text{C}$  to form a light white suspension. After cooling to room temperature, a predetermined quantity of NaH was added to the suspension to form an ionized solution. For example, in preparation of **1a** ( $[C_{60}]/[\text{OH of PVA}] = \frac{1}{100}$ ), a violet solution formed by dissolving 20 mg of  $C_{60}$  ( $2.78 \times 10^{-5}$  mol) in 30 mL toluene was added into the ionized PVA solution dropwise under vig-

orous stirring and allowed to react at room temperature for 24 h. The dark-brown solid that appeared was collected by filtration and washed with acetone. The ionized  $C_{60}$ -containing PVA products [**1a**:  $\text{PVA}(C_{60}^-Na^+)_n$ ] were separated by reprecipitating in acetone after dissolving the solids in distilled water. Other  $\text{PVA}(C_{60}^-Na^+)_n$  products **2a–4a** were prepared by similar procedures with varied  $C_{60}$  quantity ( $[C_{60}]/[\text{OH of PVA}] = \frac{1}{50}$ ,  $\frac{1}{30}$ , and  $\frac{1}{10}$  for **2a**, **3a**, and **4a**, respectively).

The ionized  $C_{60}$ -containing PVAs (**1a–4a**) were converted to **1b–4b** [ $\text{PVA}(C_{60}H)_n$ ] by stirring with an excess of cationic ion-exchange resin (Amberlite R-120: strong acid cation exchanger of the  $H^+$  form) for 1 day. The reduced  $C_{60}H$ -containing PVAs (**1b–4b**) were isolated by reprecipitating in acetone.

**1a**: Hygroscopic dark-brown solids, IR (KBr)  $\nu$  3400 ( $-\text{OH}$ ), 2900 ( $\text{C}-\text{H}$ ), 1600 (aromatic  $\text{C}=\text{C}$ ), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ). **1b**: Dark-brown solids, yield = 89.1%,  $\eta_{\text{red}} = 0.66$  dL/g ( $c = 0.2$  g/dL DMSO,  $30^\circ\text{C}$ ); IR (KBr)  $\nu$  3400 ( $-\text{OH}$ ), 2900 ( $\text{C}-\text{H}$ ), 1600 (aromatic), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ). **2a**: Hygroscopic dark-brown solids, IR (KBr)  $\nu$  3400 ( $-\text{OH}$ ), 2950 ( $\text{C}-\text{H}$ ), 1600 (aromatic), 1400 ( $-\text{CH}_2$ ), 100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ). **2b**: Dark brown solids, yield = 91.7%,  $\eta_{\text{red}} = 0.61$  dL/g ( $c = 0.2$  g/dL DMSO,  $30^\circ\text{C}$ ); IR (KBr)  $\nu$  3400 ( $-\text{OH}$ ), 2950 ( $\text{CH}$ ), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ); UV-VIS spectra (DMSO):  $\lambda_{\text{max}} = 268.5$  nm, 400–700 nm. **3a**: Hygroscopic dark-brown solids, IR (KBr)  $\nu$  3410 ( $-\text{OH}$ ), 2900 ( $\text{CH}$ ), 1600 (aromatic), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ). **3b**: Dark-brown solids, yield = 93.3%,  $\eta_{\text{red}} = 0.53$  dL/g ( $c = 0.2$  g/dL DMSO,  $30^\circ\text{C}$ ); IR (KBr)  $\nu$  3410 ( $-\text{OH}$ ), 2900 ( $\text{CH}$ ), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ); UV-VIS spectra (DMSO):  $\lambda_{\text{max}} = 263.5$  nm, 400–700 nm. **4a**: Hygroscopic dark-brown solids, IR (KBr)  $\nu$  3400 ( $-\text{OH}$ ), 2910 ( $\text{CH}$ ), 600 (aromatic), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ). **4b**: Dark-brown solids, yield = 48.3%,  $\eta_{\text{red}} = 0.38$  dL/g ( $c = 0.2$  g/dL DMSO,  $30^\circ\text{C}$ ); IR (KBr)  $\nu$  3400 ( $-\text{OH}$ ), 2900 ( $\text{CH}$ ), 1400 ( $-\text{CH}_2$ ), 1100  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ); UV-VIS spectra (DMSO):  $\lambda_{\text{max}} = 264$  nm, 400–700 nm.

### Measurement

Infrared spectra (IR) of the polymers were recorded using an FTIR spectrophotometer, model Magna-IR 550 series II from Nicolet. Ultraviolet and visible spectra was recorded using an UV-

**Table I** Preparation and Properties of PVA(C<sub>60</sub>H)<sub>n</sub>

Polymer	[C <sub>60</sub> ]/[OH]	Yield (%)	T <sub>g</sub> <sup>a</sup> (°C)	η <sub>red</sub> <sup>b</sup> (dL/g)	
				After Adding 1 mL H <sub>2</sub> O <sup>c</sup>	
<b>PVA</b>	—	—	86.5	1.97	1.96
<b>1b</b>	1/100	89.1	101.7	0.66	1.30
<b>2b</b>	1/50	91.7	102.2	0.61	0.88
<b>3b</b>	1/30	93.3	105.1	0.53	0.79
<b>4b</b>	1/10	48.3	112.6	0.38	0.57

<sup>a</sup> Glass transition temperature was measured by DSC from room temperature to 150°C at a heating rate of 10°C/min.

<sup>b</sup> Reduced viscosity (η<sub>red</sub>) was determined using an Ostwald viscometer in 0.2 g/dL DMSO at 30°C.

<sup>c</sup> It was measured immediately after adding 1 mL water to the 20 mL solution prepared for viscosity measurement.

Visible Spectrophotometer from Shimadzu, model UV-160A. The viscosities of the polymers were measured at 30°C using an Ostwald viscometer, the concentration was 0.2 g/dL in dimethyl sulfoxide (DMSO). Glass transition temperatures of **1b–4b** were determined from differential scanning calorimetric thermograms using a Shimadzu DSC-50 at a heating rate of 10°C min<sup>-1</sup> and a sensitivity of 5 mcal s<sup>-1</sup> under nitrogen purging.

### Reversible Photocrosslinking of the Copolymers

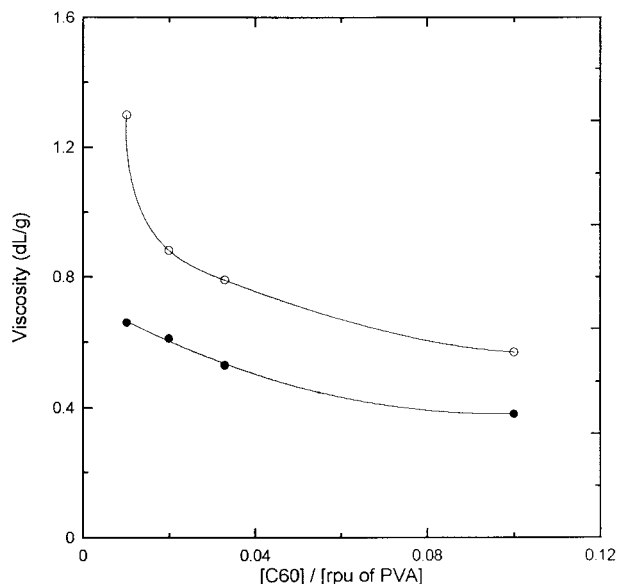
The solution used for photocrosslinking (300 nm) and photocleavage (254 nm) were prepared by dissolving 0.001 g of **1b–4b** in 50 mL DMSO. A quartz UV cell of 1 × 1 × 5 cm was filled with the DMSO solution after purging with nitrogen for 30 min. The cell was then put into a photochemical reactor, model RPR-100 from Rayonet, containing 16 UV lamps. The photocrosslinking through dimerization of pendant C<sub>60</sub>H chromophores was first conducted by irradiating with a 300 nm light. Then, after exchanging with 254 nm UV lamps, it was photocleaved symmetrically to original polymers. Photoreaction was traced by recording the absorbance change at 325 nm, which is one of the characteristic absorption of C<sub>60</sub>H chromophores, using an UV-Visible spectrophotometer. The photocrosslinking and photocleavage cycles were repeated several times to investigate their reversibility. Within the Rayonet Photochemical Chamber Reactor equipped with 16 UV lamps, their intensity readings at the reaction site are 6.17 mJ/cm<sup>2</sup> · s (300 nm) and 10.28 mJ/cm<sup>2</sup> · s (254 nm), respectively, as measured with UV meters.

## RESULTS AND DISCUSSION

### Preparation of C<sub>60</sub>-Containing PVA (Scheme 1)

Due to electronegative characteristics of C<sub>60</sub>, nucleophilic addition of alkylamine to C<sub>60</sub> has been accomplished.<sup>36</sup> Wilson et al. reported multiple addition of methoxide ions to C<sub>60</sub> and detected the odd-number methoxy derivatives of C<sub>60</sub> by electrospray ionization.<sup>37</sup> In this work, hydroxy groups of PVA were first ionized to oxy anions by NaH, followed by nucleophilic addition to C<sub>60</sub>. Ionization of PVA by a strong base NaH should increase its nucleophilicity significantly. The anion adducts are PVA(C<sub>60</sub><sup>-</sup>Na<sup>+</sup>)<sub>n</sub> formed by addition of a PVA anion to the double bonds of C<sub>60</sub>. The anion adduct is stabilized by the resonance effect of π electrons on C<sub>60</sub>. From molecular orbital concept, the σ bonds between oxygen and C<sub>60</sub> are formed through overlapping of HOMO of the oxy anion and LUMO of C<sub>60</sub>. The PVA(C<sub>60</sub><sup>-</sup>Na<sup>+</sup>)<sub>n</sub> products can be readily converted to PVA(C<sub>60</sub>H)<sub>n</sub> using a strong acid cation exchanger. Multiaddition of oxy anions to C<sub>60</sub> is possible theoretically, and will result in the formation of insoluble gels of PVA. To prevent this gelling reaction, only low C<sub>60</sub> content was employed in our experiments ([C<sub>60</sub>]/[OH of PVA] is kept below  $\frac{1}{10}$ ), as shown in Table I.

Comparing the infrared spectra of PVA(C<sub>60</sub><sup>-</sup>Na<sup>+</sup>)<sub>n</sub> with PVA, a new absorption at 1600 cm<sup>-1</sup> appears in the former. This seems to be ascribed to the absorption of C<sub>60</sub><sup>-</sup>Na<sup>+</sup> because both PVA and C<sub>60</sub> do not show absorption at 1600 cm<sup>-1</sup> (C<sub>60</sub> only exhibits absorptions at 527 cm<sup>-1</sup>, 577 cm<sup>-1</sup>, 1183 cm<sup>-1</sup>, and 1428 cm<sup>-1</sup>). Addition of oxy anions to C<sub>60</sub> destroys its I<sub>h</sub> symmetry and results in simi-



**Figure 1** Reduced viscosity of **1b-4b**: (●) 0.2 g/dL in DMSO; (○) after adding 1 mL water.

lar absorption of heteroaromatic at  $1600\text{ cm}^{-1}$ . The incorporation of  $\text{C}_{60}$  chromophores can also be ascertained by the appearance of UV absorption at ca. 260–280 nm and 400–700 nm, which are attributed to the  $\pi \rightarrow \pi^*$  transition of conjugated dienes or multienes.<sup>38</sup> Moreover, no  $\text{C}_{60}$  was extracted from **1a-4a** and **1b-4b** by toluene, which is a good solvent for  $\text{C}_{60}$ , i.e., after extraction it shows no characteristic violet color in the toluene phase. This means that most  $\text{C}_{60}$  has been consumed during reaction with PVA anions.

#### Viscosity Variation of **1b-4b** after Adding Water

The reduced viscosities ( $\eta_{\text{red}}$ ) of **1b-4b** are between 0.38 dL/g and 0.66 dL/g ( $c = 0.2\text{ g/dL}$  DMSO at  $30^\circ\text{C}$ ), which is much lower than 1.97 dL/g of the original PVA. And they decrease from 0.66 to 0.38 dL/g as  $[\text{C}_{60}]/[\text{OH of PVA}]$  is increased from 0.01 to 0.1, as shown in Table I and Figure 1. The viscosity decrease could be explained by DMSO being a poorer solvent for PVA with pendant  $\text{C}_{60}\text{H}$  groups, thus causing chain collapse from a fully expanded state. In dilute solution, hydrogen bonding should be limited and would be an intramolecular one causing the molecules to coil up. One milliliter of water was added to each solution (20 mL) after viscosity measurement, and the viscosity was remeasured under the same conditions. The remeasured viscosity increases

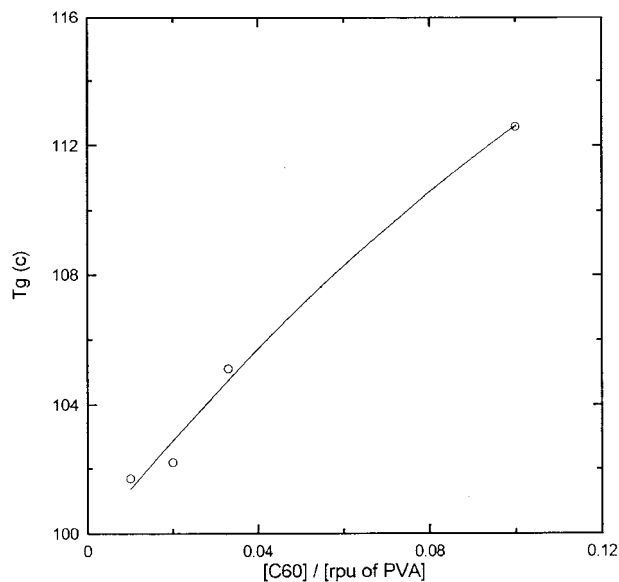
significantly (more than 0.2 dL/g) for both samples. However, no viscosity increase was observed for pure PVA after addition of 1 mL of water. It seems that water addition yields a better solvent combination to extend the coiled chain of **1b-4b**.

#### Glass Transition Temperature of **1b-4b**

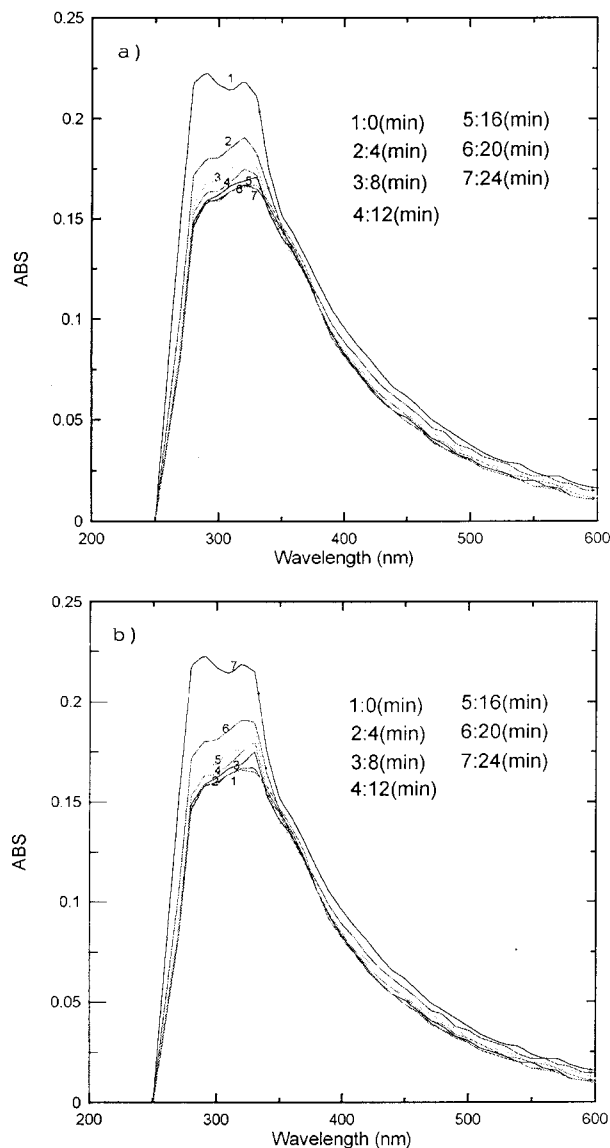
Bulky pendant groups usually raise the glass transition temperature of a polymer by hindering its segmental rotation. Caged  $\text{C}_{60}$  is a rigid buckyball with a diameter of about 7 angstrom, which would not be changed significantly after attaching to PVA pendant groups. As shown in Figure 2, the  $T_g$ s of **1b-4b** increase from 101.7 to  $112.6^\circ\text{C}$  as  $[\text{C}_{60}]/[\text{OH of PVA}]$  is increased from  $\frac{1}{100}$  to  $\frac{1}{10}$ . The  $T_g$  of PVA is around  $86.5^\circ\text{C}$ , which is much lower than those of **1b-4b**. Clearly, addition of  $\text{C}_{60}\text{H}$  to PVA prevents its segmental motion and thus increases its  $T_g$ .

#### Reversible Photoreaction of **1b-4b**

In general, the reversibility of compounds containing photoreactive double bonds conjugated with aromatic a  $\pi$ -electron cloud can be traced by their peak absorption variation during reaction. As shown in Figure 3(a), upon irradiation with 300 nm light, the absorption of **1b** at 325 nm decreases gradually to an equilibrium value, which should be due to formation of cyclobutane through dimerization of  $\text{C}_{60}\text{H}$  chromophores (pho-



**Figure 2** Dependence of  $T_g$  on  $\text{C}_{60}$  concentration.



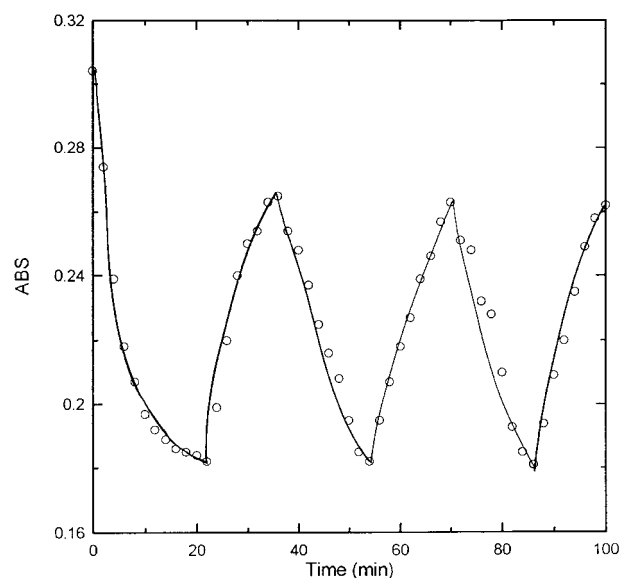
**Figure 3** UV spectral variation of **1b** in DMSO (a) Under 300 nm light, and then (b) under 254 nm light.

tocrosslinking). Followed by irradiating with 254 nm light [Fig. 3(b)], the dimers are split symmetrically to the original C<sub>60</sub>H chromophores (photocleavage) as shown in Scheme 1. Clearly, it shows very good photoreaction reversibility in **1b**. Using this characteristics, reversible photoreaction of **1b–4b** can be traced by recording their absorption variation at 325 nm. Irradiation of **1b** with 350 nm light also results in a gradual decrease in absorption at 325 nm. However, the reaction is slow and it takes about 98 min to reach an asymptotic minimum absorption compared to

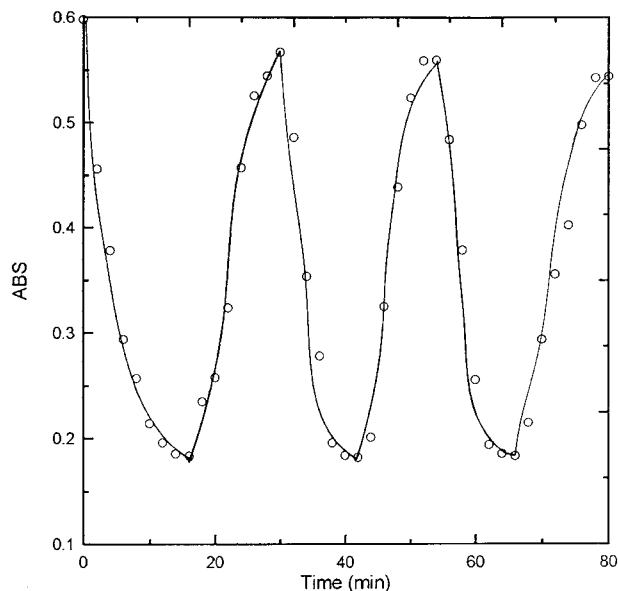
about 13 min under 300 nm light. Therefore, the 300 nm UV light is employed as a source of irradiation.

As shown in Figure 4, irradiation of **1b** with 300 nm light results in a quick absorption decrease from 0.304 to an asymptotic value of 0.181 within 22 min. Subsequent irradiation with 254 nm UV light, the absorption increases quickly to 0.265, which is smaller than the original 0.304. For convenience, successive photocrosslinking with 300 nm light and photocleavage with 254 nm is defined as one cycle. Therefore, in the first cycle the maximum absorbance cannot restore to its original absorbance of 0.304 under photo splitting at 254 nm, which is very similar to that of coumarin dimer chromophores.<sup>30</sup> This can be explained by simultaneous occurrence of splitting of C<sub>60</sub>H dimers and dimerization of C<sub>60</sub>H under 254 nm light, i.e., it is an equilibrium reaction. From the second cycles on, the maximum and minimum absorptions fluctuate between ca. 0.265 and ca. 0.181, suggesting that photocrosslinking of the C<sub>60</sub>-containing PVAs is quite reversible. This is the first report about reversible photoreaction of C<sub>60</sub>-containing polymers.

For **2b**, the absorbance decreases from 0.598 to 0.180 upon irradiation with a 300 nm light and increases again to about 0.575 under a 254 nm light, as shown in Figure 5. The maximum absorbance of the second and third cycles degenerates



**Figure 4** Absorbance at 325 nm versus irradiation time for **1b** in DMSO (photocrosslinking: 300 nm, photocleavage: 254 nm).



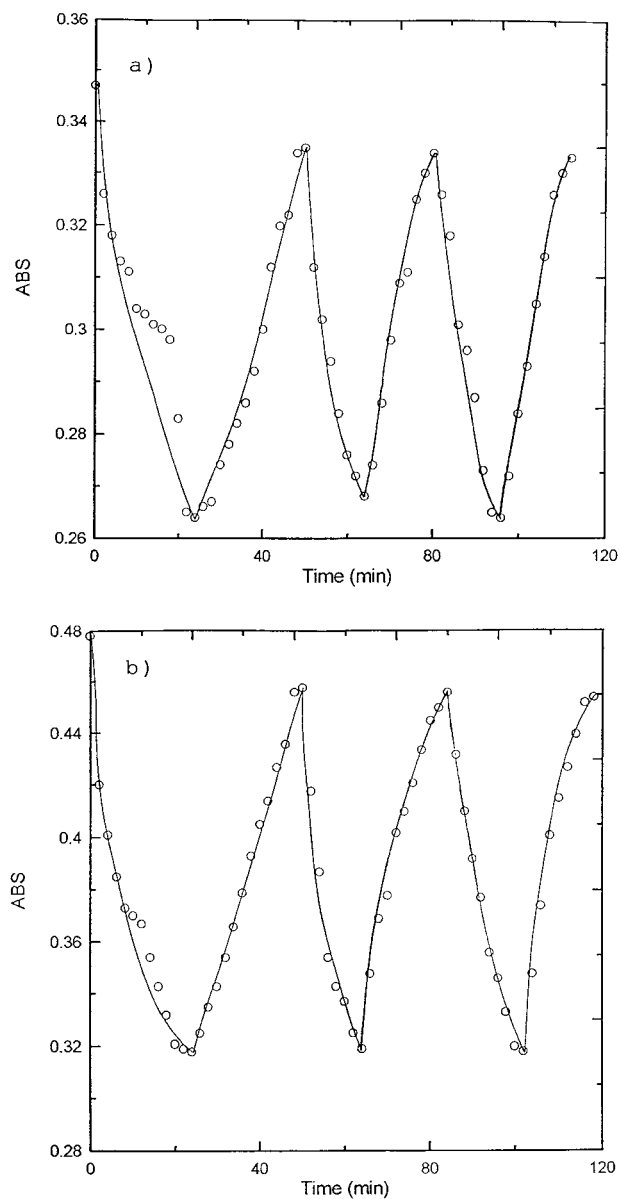
**Figure 5** Absorbance at 325 nm versus irradiation time for **2b** in DMSO (photocrosslinking: 300 nm, photocleavage: 254 nm).

slightly to 0.572 and 0.561, respectively. However, the minimum absorbance remains almost the same at about 0.180. Polymers **3b** and **4b** exhibit similar photoreaction behaviors, as shown in Figure 6. For **3b**, the absorbance is 0.348 for the as-prepared solution, and it fluctuates between 0.263 and 0.335 from the second cycles on [Fig. 6(a)]. For **4b**, the maximum is 0.478 for the first cycle and it fluctuates between 0.318 and 0.456 in the following two cycles. Therefore, both **1b-4b** show quite good photoreaction reversibility in the observed three cycles.

## CONCLUSIONS

Poly(vinyl alcohol)s with pendant  $C_{60}^-Na^+$  groups (**1a-4a**) have been prepared by electrophilic addition of  $C_{60}$  to poly(vinyl alcohol) anions, which was formed *in situ* by adding NaH to a PVA solution in DMF. The **1a-4a** were converted to  $PVA(C_{60}H)_n$  (**1b-4b**) by reacting with cationic exchange resin (strong acid exchanger of  $H^+$  form). Both **1a-4a** and **1b-4b** have been extracted with toluene, which is a good solvent for  $C_{60}$ , and no characteristic violet color transfer to toluene was observed. The viscosity of  $PVA(C_{60}H)_n$  decreases

with  $C_{60}$  content, which has been explained by the hindrance of  $C_{60}$  to hydrogen bonding between PVAs. The  $T_g$ s of  $PVA(C_{60}H)_n$  increase with  $C_{60}$  contents. Under irradiation with a 300 nm light, the absorbance (of **1b-4b** at 325 nm in DMSO) decreases readily to an asymptotic minimum. Followed with 254 nm irradiation, it increases again to a maximum, which is smaller than the as-prepared solution. From the second cycles on, the absorbance fluctuates between a minimum and a



**Figure 6** Absorbance at 325 nm versus irradiation time for (a) **3b** and (b) **4b** in DMSO (photocrosslinking: 300 nm, photocleavage: 254 nm).

maximum and shows good reversibility. These have been attributed to reversible [2 + 2] photodimerization and photocleavage of the pendant C<sub>60</sub>H chromophores under 300 and 254 nm light, respectively.

The authors thank National Science Council of the Republic of China for financial aid (NSC 85-2216-E-006-050).

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