

# Valence isomerization of norbornadiene in polymer systems for solar energy storage

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Received 10 October 1995; accepted 17 November 1995

## Abstract

Two new kinds of polymer, copolymer  $P_{1-2}$  and homopolymer  $P_3$ , containing norbornadiene and carbazole pendants were synthesized. The photoinduced valence isomerizations of norbornadiene to quadricyclane in polymer  $P_{1-2}$  and  $P_3$  were achieved by irradiation of visible light (wavelength, greater than 350 nm) and an electron transfer mechanism was proposed. The back isomerization from quadricyclane to norbornadiene was also carried out for the polymer systems.

**Keywords:** Polymers; Norbornadiene pendants; Carbazole pendants; Valence isomerization; Electron transfer

## 1. Introduction

Valence isomerization of norbornadiene to quadricyclane is one of the most promising systems for solar energy conversion and storage. Since the emission of sunlight falls mainly in the visible region (300–700 nm), norbornadiene itself cannot harvest solar energy directly. To utilize solar energy more efficiently and to promote the quantum yield of photoinduced isomerization, a number of investigations have been carried out into the use of sensitizers, the introduction of chromophores and the synthesis of norbornadiene-sensitizer binary compounds etc. [1–3]. Most popular sensitizers for norbornadiene isomerization are the triplet sensitizers (such as benzophenone, acetophenone and Michler's ketone) via the mechanism of triplet–triplet energy transfer [4]. Afterwards, chemists [5,6] used the electron transfer of singlet excited sensitizers (such as polycyclic aromatic hydrocarbons, acridine dyes and carbazole) to initiate the photoinduced valence isomerization of norbornadiene to quadricyclane and have made progress. In order to put this into practical application, some chemists make use of polymeric sensitizers [7] and some synthesize norbornadiene polymers [8] to investigate the photoinduced valence isomerization in polymer film.

In this paper, two kinds of polymer  $P_{1-2}$  and  $P_3$  (Scheme 1) containing norbornadiene and carbazole pendants were designed and synthesized, and polymer  $P_2$ , polynorbornadiene

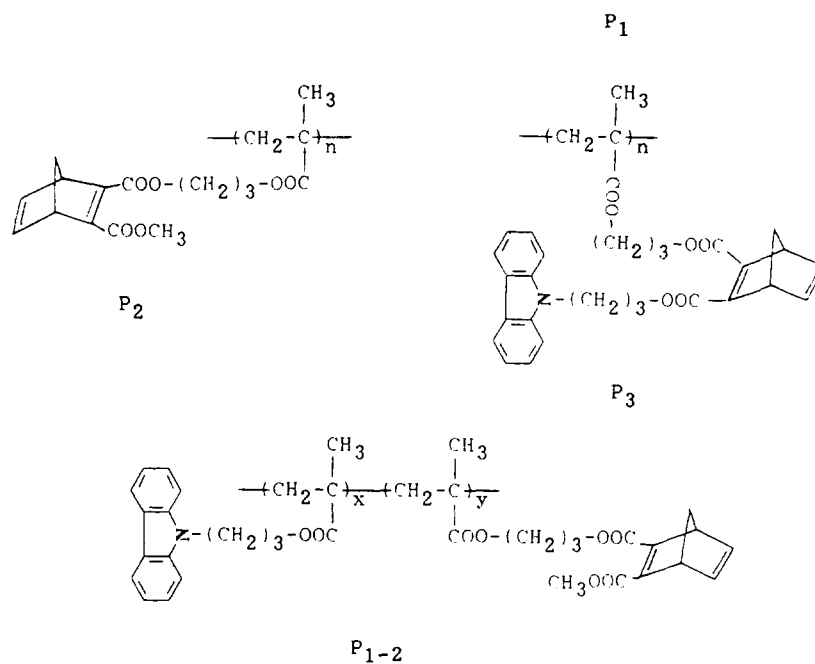
ene methyl acrylate, was also prepared for comparison.  $P_{1-2}$  is a copolymer formed from monomer-1- and monomer-2-bearing carbazole and norbornadiene moiety respectively.  $P_3$  is a polymer of monomer 3 which links carbazole and norbornadiene in a non-conjugated manner. The photoinduced valence isomerization for all three kinds of polymer,  $P_{1-2}$ ,  $P_3$  and  $P_2$ , can occur by irradiation of UV light (wavelength, less than 350 nm). When irradiated by visible light (wavelength, greater than 350 nm), only the valence isomerization of  $P_{1-2}$  and  $P_3$  takes place and an electron transfer mechanism was proposed. Using cobalt porphyrin or trifluoroacetic acid as catalyst, the back isomerizations of quadricyclane to norbornadiene proceeded smoothly and the energy stored in high strain quadricyclane was released as heat energy in this step. Thus a whole process containing photochemical energy storage and catalytic energy release was performed completely in polymer systems.

## 2. Experimental details

### 2.1. Materials

*N*-methylcarbazole was synthesized in our laboratory. Acetonitrile (E. Merck, Darmstadt; analytic grade reagent) was dried on KOH before the experiments. Various norbornadiene derivatives (**2**, **3**, **Ia**, **IIa** and **IIIa**; see Scheme 1 and Scheme 3) were synthesized as described in the literature [9,10].

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Scheme 1.

## 2.2. Synthesis of polymers

### 2.2.1. Monomers

Monomer 1 (Scheme 3) was obtained through the reaction of **1** and carbazole in the presence of sodium hydroxide and hexadecyl trimethyl ammonium bromide (CTAB) used as phase transfer catalyst in the mixed solvent of chloroform and water [11]. Using the same method, monomer 2 and monomer 3 were also synthesized by reaction of **2** and **3** with **1** respectively. All monomers were identified by IR, <sup>1</sup>H nuclear magnetic resonance (NMR), mass spectroscopy techniques and purified by chromatography.

### 2.2.2. Homopolymer P<sub>3</sub>

A solution of monomer **3** (1.0 g) and azobisisobutyronitrile (AIBN) (0.06 g) in tetrahydrofuran (10 ml) was stirred in an oil bath (50 °C) for 72 h under an N<sub>2</sub> atmosphere, and the resulting polymer was precipitated into petroleum ether to afford a white powder. Under this polymerization condition, no gel was formed. Information provided by the IR and <sup>1</sup>H NMR methods indicated that the double bonds of the norbornadiene pendants did not participate in the polymerization. P<sub>1</sub> and P<sub>2</sub> were also prepared by using the same method.

### 2.2.3. Copolymer P<sub>1-2</sub>

0.542 g (1.64 × 10<sup>-3</sup> mol) of monomer **2** and 0.480 g (1.64 × 10<sup>-3</sup> mol) of monomer **1** in 8.0 ml of tetrahydrofuran were polymerized in an N<sub>2</sub> atmosphere by using 0.06 g of AIBN as initiator (50 °C; 72 h). The resulting polymer P<sub>1-2</sub> was precipitated into petroleum ether. The value of x:y measured with the UV spectrum method was around 1:1.

## 2.3. Apparatus

The absorption spectra were taken with a Hewlett–Packard 8451A spectrophotometer. IR spectra were run on a Perkin–Elmer 983G grating spectrophotometer using KBr pellets. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrofluorometer. Fluorescence lifetimes were measured on a Horiba NAES-1100 single-photon-counting nanosecond fluorescence spectrometer. Chemically induced dynamic nuclear polarization (CIDNP) experiments were carried out with a slightly modified Bruker <sup>1</sup>H NMR spectrometer (operating at 80 MHz).

## 2.4. Irradiation

The irradiations of polymer P<sub>1-2</sub>, P<sub>3</sub> and P<sub>2</sub> were carried out at a distance of 5 cm from a 400 W medium pressure mercury lamp under a nitrogen atmosphere. Light with a wavelength greater than 350 nm was obtained by setting a filter (Corning 0–52) in front of the lamp.

## 2.5. Catalytic reaction

A catalytic amount of trifluoroacetic acid or cobalt porphyrin was added to the solution of P<sub>3</sub>, P<sub>1-2</sub> or P<sub>2</sub> in benzene which had been irradiated thoroughly; then the reverse valence isomerization of quadricyclane pendants in these polymers was measured with an IR spectrophotometer.

## 3. Results and discussion

### 3.1. Photoisomerization of polymers

The UV spectrum of the P<sub>3</sub> film and the change in the IR spectrum of P<sub>3</sub> by irradiation with the light above a wave-

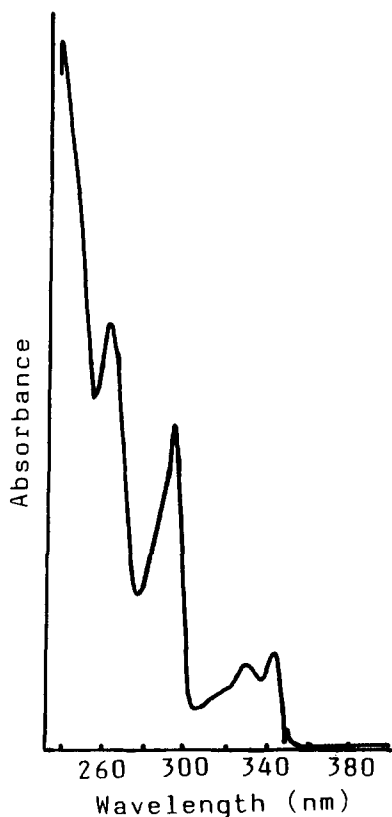


Fig. 1. UV spectrum of  $P_3$  film.

length of 350 nm are shown in Figs. 1 and 2 respectively. Fig. 2(a) shows the IR spectrum of  $P_1$  in the range 1700–1500  $\text{cm}^{-1}$  and the absorption peaks at 1622 and 1595  $\text{cm}^{-1}$  are ascribed to the skeletal vibration absorption of carbazole pendants. Because there are double bonds of norbornadiene in  $P_3$ , the intensity of the absorption at 1622  $\text{cm}^{-1}$  is higher than that at 1595  $\text{cm}^{-1}$  as shown in Fig. 2(b). After irradiation by light above the wavelength of 350 nm (in a film state or in solution), the intensity of the absorption at 1622  $\text{cm}^{-1}$  distinctly decreased as shown in Fig. 2(c), which indicated that the irradiation caused the disappearance of double bonds and the norbornadiene pendants had been converted into corresponding quadricyclane pendants (Scheme 2). Although the photoisomerization of  $P_{1-2}$  can also take place under the same irradiation condition (wavelength, greater than 350 nm), the difference between the reaction rates of  $P_3$  and  $P_{1-2}$  is distinct. If the photoisomerization quantum yield of  $P_3$  is assumed to be one unit, the photoisomerization quantum yield of  $P_{1-2}$  is only 0.41. Isomerization of norbornadiene pendants in  $P_3$  and  $P_{1-2}$  to the corresponding quadricyclane is due to the introduction of carbazole chromophores as pendants in polymers.

Under the same irradiation condition, the IR spectrum of  $P_2$  which only has norbornadiene as a pendant did not have any changes either in the film state or in solution. The photoisomerization of  $P_2$  could not proceed, because  $P_2$  does not absorb the light above 350 nm. When  $P_2$  was irradiated using a medium pressure mercury lamp with a quartz reactor, the

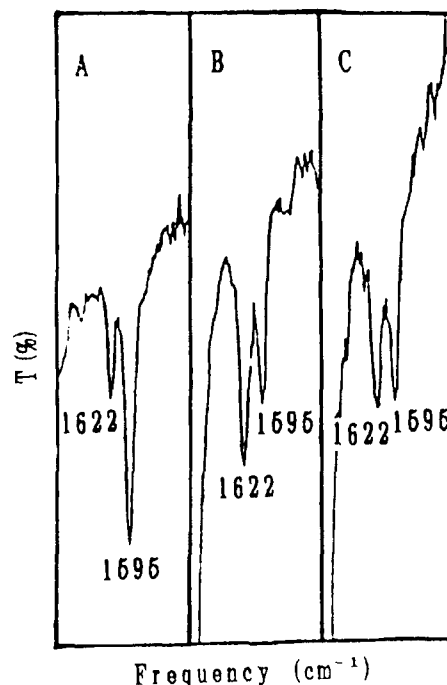


Fig. 2. Change in IR spectrum of  $P_3$  after irradiation with the light of wavelength greater than 350 nm: (a) IR spectrum of  $P_1$ ; (b) IR spectrum of  $P_3$ ; (c) IR spectrum of  $P_3$  after irradiation.

characteristic absorptions of norbornadiene at 3070  $\text{cm}^{-1}$  ( $\nu_{(\text{C-H})}$ ), 1623  $\text{cm}^{-1}$  ( $\nu_{(\text{C=C})}$ ) and 700  $\text{cm}^{-1}$  ( $\delta_{(\text{C-H})}$ ) disappeared completely, which proved that the valence isomerization of the norbornadiene to the quadricyclane unit in  $P_2$  had occurred.

### 3.2. The mechanism for photosensitized isomerization of norbornadiene

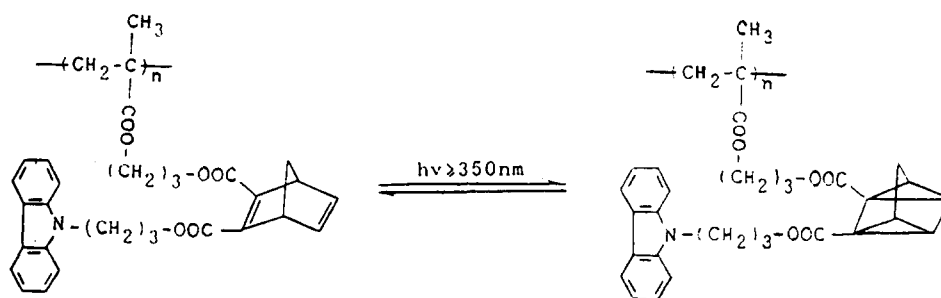
#### 3.2.1. Fluorescence quenching

In order to clarify the mechanism for the photosensitized isomerization of norbornadiene pendants in  $P_{1-2}$  and  $P_3$ , several norbornadiene derivatives (**Ia**, **IIa** and **IIIa** in Scheme 2), which serve as electron acceptors, were selected for quenching study of *N*-methylcarbazole.

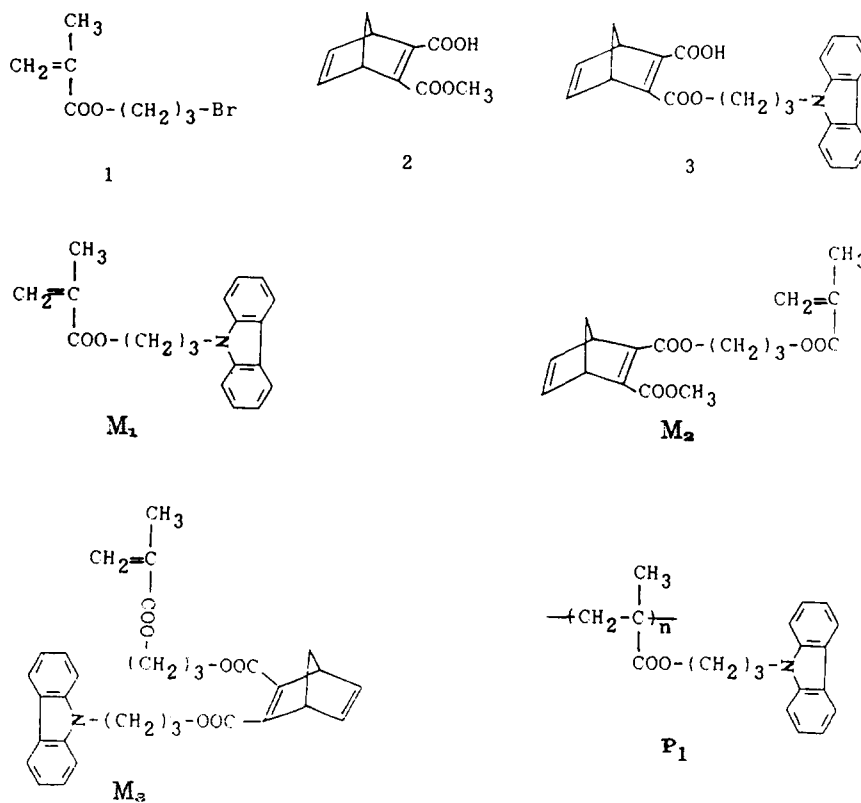
The fluorescence intensity  $I$  and fluorescence lifetime  $\tau$  are related to the quenching rate constant  $k_q$  and the concentration  $[Q]$  of quencher by the Stern–Volmer equation ([12], p. 247)

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \quad (1)$$

where  $I_0$  and  $\tau_0$  are the fluorescence intensity and fluorescence lifetime respectively in the absence of quencher. In the quenching experiments mentioned above, all data followed the Stern–Volmer equation and gave straight lines with intercepts of unity. From the slopes  $k_q \tau_0$  of these straight lines and the lifetime of *N*-methylcarbazole (14.8 ns), the fluorescence quenching rate constants  $k_q$  obtained range from  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  upwards (shown in Table 1), approaching the diffusion-



Scheme 2.



Scheme 3.

Table 1  
Quenching rate constants  $k_q$

	$k_q \times 10^{-10}$ (1 mol <sup>-1</sup> s <sup>-1</sup> )	
	From $I_0/I$	From $\tau_0/\tau$
Ia	2.40	2.30
IIa	4.00	
IIIa	1.30	1.20

controlled limit, as expected for efficient (exothermic) electron transfer.

The fluorescence lifetimes of *N*-methylcarbazole in the presence of quenchers with different concentrations have been measured. The plots of  $\tau_0/\tau$  vs.  $[Q]$  are also predicted to yield a straight line of slope equal to  $k_q\tau_0$  and intercept equal to 1. The  $k_q$  values (in Table 1) obtained from  $\tau_0/\tau$  are consistent with those from  $I_0/I$ . This implies that the fluores-

cence quenching of sensitizer by quencher is a dynamic process, i.e. via electron transfer quenching.

The efficiencies of fluorescence quenching of carbazole unit (electron donor D) by norbornadiene unit (electron acceptor A) in  $P_{1-2}$  and  $P_3$  were 79.4% and 98.8% respectively. The electron transfer rate constants  $k_{et}$  in  $P_{1-2}$  and  $P_3$  calculated from the following equation were  $2.60 \times 10^8$  s<sup>-1</sup> and  $5.56 \times 10^9$  s<sup>-1</sup> respectively:

$$k_{et} = \frac{1}{\tau} - \frac{1}{\tau_0} \quad (2)$$

where  $\tau_0$  (14.8 ns) is the lifetime of the model compound (methyl carbazole) in which no electron transfer occurs, and  $\tau$  is the lifetime of carbazole chromophore in  $P_{1-2}$  (3.05 ns) or  $P_3$  (0.18 ns) where photoinduced electron transfer takes place.

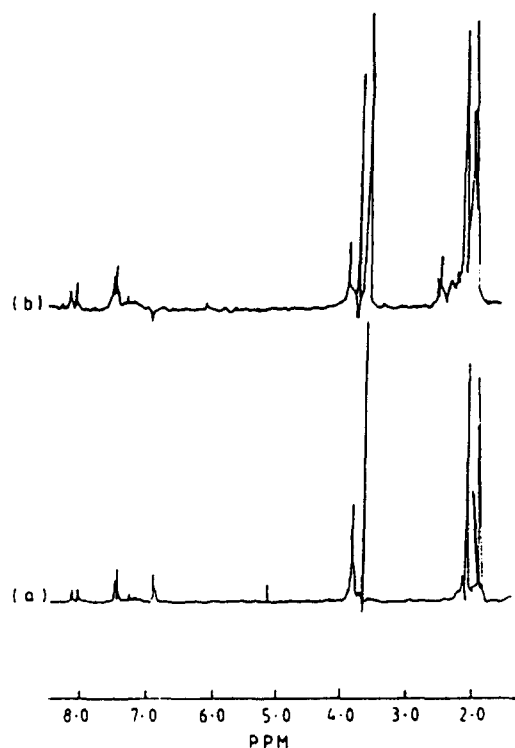


Fig. 3.  $^1\text{H}$  NMR spectra (80 MHz) of  $\text{CH}_3\text{Cz}$  ( $7 \times 10^{-3}$  M) and **IIIa** ( $2 \times 10^{-2}$  M) in acetonitrile- $d_3$  (a) before irradiation and (b) during irradiation.

The fluorescence quenching efficiency, the electron transfer rate constant and the photoisomerization quantum yield of  $\text{P}_3$  are all greater than those of  $\text{P}_{1-2}$ . Therefore it can be deduced that the isomerization is through an electron transfer reaction and it is more favourable in the polymer with covalently bonded D–A as pendants ( $\text{P}_3$ ) than in that with separate D and A as pendants ( $\text{P}_{1-2}$ ).

### 3.2.2. Chemically induced dynamic nuclear polarization experiments

The CIDNP method has proved to be a valuable tool for the investigation of photoinduced isomerizations that proceed via electron transfer and radical-ion intermediates.

The solution of **IIIa** ( $2 \times 10^{-2}$  M in  $\text{CD}_3\text{CN}$ ) was irradiated in the probe of a  $^1\text{H}$  NMR spectrometer in the presence of *N*-methylcarbazole ( $7 \times 10^{-3}$  M). A characteristic CIDNP signal was observed. Olefinic protons of norbornadiene (**IIIa**) were observed in emission. The corresponding pro-

tons of the quadricyclane isomer exhibited a complementary polarization, namely enhanced absorption (Fig. 3).

No nuclear polarization could be detected for the olefinic protons of either **IIIa** or **IIIb** or for the protons of *N*-methylcarbazole. Irradiation of **IIIa** in the absence of an *N*-methylcarbazole resulted in slow photoisomerization, but no CIDNP was observed. Photolysis in the presence of typical triplet photosensitizers (such as benzophenone) brought about efficient isomerization; also, no nuclear polarization was observed.

The results of CIDNP experiments are consistent with the existence of intermediates of radical-ion pairs and a triplet recombination mechanism. According to the well-known CIDNP Kaptein rules ([12], p. 284),

$$\begin{aligned} \Gamma(\text{net polarization}) &= \mu \epsilon \Delta g \alpha_H \\ &= +A (\text{enhanced absorption}) - E (\text{emission}) \end{aligned}$$

The net polarization effect depends on four parameters: the initial spin multiplicity  $\mu$  of the radical pair, the mode  $\epsilon$  of product formation, the sign of the difference  $\Delta g$  between isotropic  $g$  factors of the individual radicals and the sign of the hyperfine coupling constant (HFC)  $a_H$  for the magnetic nucleus under observation.

In our reactions, all products are expected to be formed within the cage ( $\epsilon > 0$ ). The  $g$  factors for the hydrocarbon radical cations are to be smaller than the value for  $\text{N}^-$  which bears electron-withdrawing substitutes ( $\Delta g > 0$ ). The signs for the proton HFC of the radical anion of N are not known, but all seem to have the same signs and must therefore be positive ( $a_H > 0$ ). Thus  $\mu < 0$  implies singlet radical-ion pair recombination which favours N;  $\mu > 0$  implies triplet radical-ion pair recombination which favours Q.

### 3.2.3. Thermodynamic discussion

The free-energy change involved in an electron transfer process can be calculated by the Rehm–Weller equation [13]:

$$\Delta G = 23.06 \left( E(D-D^+) - E(A^- - A) \frac{-e_0^2}{\epsilon r} - \Delta E_{0,0} \right) \quad (3)$$

Table 2 indicates the redox potentials and excitation energies for *N*-methylcarbazole and its quenchers,  $\Delta G$  values and the radical-ion pair energies for carbazole–norbornadiene ( $\text{S}^+ - \text{N}^-$ ). From Table 2, it shows that  $\Delta G$  values are all negative. This means the electron transfers from the

Table 2  
Redox potentials, excitation energies,  $\Delta G$  values and ion pair energy

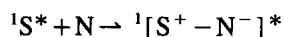
	$E(D-D^+)$ (V)	$E(A^- - A)$ (V)	$E_S$ (kcal mol $^{-1}$ )	$E_T$ (kcal mol $^{-1}$ )	$\Delta G$ (kcal mol $^{-1}$ )	$G(\text{S}^+ \cdots \text{N}^-)^a$ (kcal mol $^{-1}$ )
$\text{CH}_3\text{Cz}$	1.10		83.2	71.5		
<b>Ia</b>		−1.40		53	−26.98	56.3
<b>IIa</b>		−1.25		53	−30.44	52.8
<b>IIIa</b>		−1.67		53	−20.75	62.5

<sup>a</sup> Ion pair energies were calculated from  $G = 23.06 [E(D-D^+) - E(A^- - A) - e^2/a\epsilon]$ .

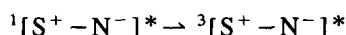
*N*-methylcarbazole to norbornadiene derivatives are exothermic, or efficient. Energetic parameters show that the radical-ion pair energies are all higher than the triplet energies of norbornadiene derivatives and lower than that of *N*-methylcarbazole. Thus norbornadiene triplet could only be directly formed via recombination of radical ion pairs.

From fluorescence quenching, CIDNP experiment and thermodynamic discussion, the mechanism of valence isomerization for P<sub>1-2</sub> and P<sub>3</sub> under the sensitization of *N*-methylcarbazole can be deduced to be as follows:

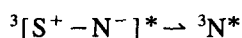
(a) electron transfer



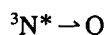
(b) intersystem crossing



(c) recombination



(d) valence isomerization



### 3.3. Isomerization of quadricyclane to norbornadiene

Generally, metalloporphyrins were often utilized as catalysts in the isomerization of quadricyclane to norbornadiene. Sometimes, proton acids could also be used as catalysts for some quadricyclane derivatives bearing a carbonyl group [14]. In this experiment, by using a catalytic amount of cobalt porphyrin or trifluoroacetic acid, the isomerizations of quad-

ricyclane pendants of irradiated P<sub>1-2</sub>, P<sub>3</sub> and P<sub>2</sub> proceeded totally smoothly at ambient temperature. Thus a whole process containing photochemical energy storage and catalytic energy release was performed completely in polymer systems.

### Acknowledgments

The authors would like to acknowledge the financial assistance from the NNSFC and Bureau of Basic Research, CAS.

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