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Rikiya Sato[a]; Hisashi Takeuchi[a]; Makoto Takeishi[a]
[a] Department of Materials Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan

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PHOTOSENSITIZED DEGRADATION OF POLY(α-CHLOROACRYLONITRILE) UNDER OXYGEN

RIKIYA SATO,* HISASHI TAKEUCHI, and MAKOTO TAKEISHI

Department of Materials Science and Engineering
Yamagata University
Yonezawa, Yamagata 992, Japan

ABSTRACT

Poly(α-chloroacrylonitrile)(PCAN) degraded upon irradiation with a xenon lamp under oxygen in the presence of 9,10-dicyanoanthracene (DCA) and *trans*-stilbene (TS), and a similar degradation was observed for the reaction of the polymer with potassium superoxide (KO_2). The IR spectra of the polymers recovered in both cases were almost the same. The mechanism of the photodegradation of PCAN was interpreted as follows: excited DCA accepts an electron from TS and the radical anion of DCA formed transfers an electron to oxygen, generating "superoxide anion ($O_2^{\cdot-}$)," which reacts with PCAN to decompose the polymer.

INTRODUCTION

We have already reported the reductive decomposition of poly(α-chloroacrylonitrile)(PCAN) during reactions with electron-donating nucleophiles or reduction with zinc in the presence of methyl viologen as an electron-transfer catalyst in which decomposition took place via an initial electron transfer from the reducing agents to the polymer [1]. In this paper we wish to report the photosensitized degradation of the polymer via a photoinduced electron transfer to oxygen.

Photodecomposition of polymers is expected to solve the problems of plastics waste; such photoreactions are accelerated by photoinitiators which yield free radicals and initiate the radical reaction to decompose the polymers [2, 3]. Photosensitizers also enhance the photodecomposition of polymers in the presence of oxygen by which singlet oxygen generated by energy transfer from excited sensitizers causes the oxidative degradation of the polymers [4, 5].

In the case of PCAN, singlet oxygen with an electrophilic character seems difficult to react with the polymer because of its electron-withdrawing groups in the main chain. Nevertheless, photosensitized degradation of the polymer was observed in the presence of a triplet sensitizer under oxygen. We investigated the mechanistic role of oxygen in this reaction.

EXPERIMENTAL

Materials

Acetonitrile (special grade supplied by Kanto Chemical Co.) was refluxed over P_2O_5 overnight and distilled before use. Dimethylsulfoxide (DMSO) (reagent grade supplied by Kanto Chemical Co.) was refluxed over calcium hydride overnight and distilled under reduced pressure before use. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used without further purification (special-grade reagent supplied by Aldrich Chemical Co.). All other special-grade reagents were used without further purification. α-Chloroisobutylonitrile (α-CIBN) was synthesized by chlorination of isobutylonitrile using phosphorous pentachloride [6].

Preparation of PCAN

Freshly distilled monomer was polymerized with potassium persulfate in water under nitrogen. The powdered polymer which precipitated was filtered and washed successively with water and methanol, and the polymer was purified by reprecipitation with acetone-methanol. The solution viscosities of PCAN obtained are given in Table 1. PCAN III ($\overline{M}_n = 3.5 \times 10^5$) was used for photodegradation.

DCA-Sensitized Photoreaction of PCAN

In a typical procedure, PCAN (3 mmol), *trans*-stilbene (TS, 0.6 mmol), and dicyanoanthracene (DCA, 0.03 mmol) were dissolved in acetonitrile (10 mL) in a Pyrex tube, oxygen was bubbled into the solution, and the tube was stoppered. The

TABLE 1. Polymerization of α-Chloroacrylonitrile[a]

PCAN	CAN, g	Water, mL	Conversion, %	η_{inh}, dL/g[b]
I	18	80	87	2.22
II	22	90	66	2.23
III	42	170	93	3.27
IV	55	220	83	2.88

[a] $K_2S_2O_8$, 2 mol%, 45°C, 48 hours.
[b] 0.5 g/dL in DMF at 30°C.

tube was irradiated with a 500-W xenon lamp (λ > 320 nm) for a given time at 20°C. After reaction, the solution was poured into methanol to deposit the resulting polymer which was collected on a glass filter.

Reaction of PCAN with KO_2

DMSO (10 mL), PCAN (3.3 mmol), and 18-crown-6 ether (0.06 mmol) were placed in a three-necked flask, and the mixture was stirred for 5 minutes with a magnetic stirrer. After the polymer had dissolved, KO_2 (0.6 mmol) was added to the solution and stirring was continued for 1 hour at room temperature (~20°C). After reaction, the polymer obtained was separated out as above.

Reaction of α-ClBN with KO_2

α-ClBN (6.7 mmol), 18-crown-6 ether (2 mmol), and DMSO (20 mL) were placed in an Erlenmeyer flask and stirred for 5 minutes with a magnetic stirrer at room temperature (~20°C). To the solution was added KO_2 (20 mmol) and stirring was continued for 1 hour. After reaction, the solution was poured into water and the product was extracted with ether. The extract was dried over magnesium sulfate and the products were separated by column chromatography using silica gel and benzene as an eluent.

Molecular Weight Measurement

Number-average molecular weights of the polymers were determined by gel permeation chromatography on a Tri-Rotar-III (Japan Spectroscopic Co.) using polystyrene standards.

ESR Measurement

ESR measurement were carried out using 5,5-dimethyl-1-pyrolline-*N*-oxide (DMPO) as a spin trap reagent. After DCA and TS were dissolved in acetonitrile, the solution was saturated with oxygen. Then DMPO was added to the solution and the mixture was irradiated with a 1-kW xenon lamp. ESR spectra were recorded on a JES-FE3X (Jeol) spectrometer.

RESULTS AND DISCUSSION

DCA-Sensitized Photodegradation of PCAN

PCAN solutions in acetonitrile containing DCA and/or TS were irradiated, and the results of photodegradation of the polymer are shown in Table 2. The decrease in molecular weight of the polymer recovered after reaction was remarkable only when both DCA and TS were present in the solution under oxygen, whereas gelation occurred under nitrogen. The dependence of the photodegradation of PCAN on the concentrations of DCA and TS is shown in Table 3.

The molecular weight of the resulting polymer decreased with increasing concentrations of DCA and TS, and the number-average values reached an order of

TABLE 2. DCA-Sensitized Photodegradation of PCAN[a]

Run	DCA, mmol	ST, mmol	Atmosphere	Yield,[b] %	η_{inh},[c] dL/g	$\overline{M}_n \times 10^{-4}$
1	–	–	O_2	90	2.91	13
2	0.02	–	O_2	91	2.47	11
3	–	0.2	O_2	90	2.34	11
4	0.02	0.2	O_2	98	1.01	2
5	0.02	0.2	N_2	100	Gel	–

[a] PCAN (III), 2 mmol; acetonitrile, 10 mL; 15 °C, 3 hours.
[b] Precipitated in methanol.
[c] 0.5 dL/g in DMF at 30 °C.

10^3. The changes in the inherent viscosity of the polymer obtained and the decreasing yield are shown in Fig. 1 as a function of reaction time.

During a 9 hour reaction, the inherent viscosity decreased from 2.72 to 0.24, indicating that degradation of PCAN occurred; in this case the yield was 60%. The decrease in weight of the recovered polymer after photoreaction suggests that PCAN degraded to methanol-soluble oligomers.

Reaction of PCAN with KO_2

It has been reported that superoxide anion ($O_2^{\cdot -}$) is generated in a photoreaction system composed of DCA, ST, and oxygen [7]. In this reaction ST is an electron donor and excited DCA is an electron mediator, as shown in Scheme 1.

In order to examine whether the generation of $O_2^{\cdot -}$ caused the photodegradation of the polymer in our case, a spin-trapping technique was used. In the ESR spectrum of the reaction solution containing DMPO, which traps the radical anion and other radicals, the absorption bands due to the adduct of DMPO—OOH can

TABLE 3. Effects of DCA and TS on the Photodegradation of PCAN under Oxygen[a]

Run	DCA, mmol	TS, mmol	Yield,[b] %	η_{inh},[c] dL/g	$\overline{M}_n \times 10^{-4}$
1	0.02	0.1	96	1.65	4
2	0.02	0.2	98	1.01	2
3	0.02	0.4	98	0.52	0.8
4	0.02	0.8	99	0.51	0.8
5	0.04	0.2	97	0.48	0.8

[a] PCAN (III), 2 mmol; acetonitrile, 10 mol; room temperature, 3 hours.
[b] Precipitated in methanol.
[c] 0.5 g/dL in DMF at 30°C.

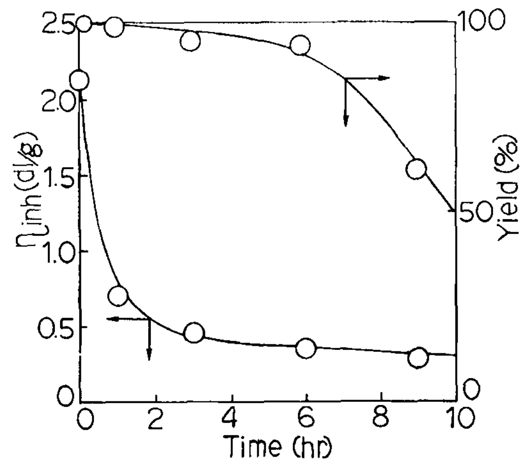


FIG. 1. DCA-sensitized photodegradation of PCAN (I) in the presence of *trans*-stilbene under oxygen. PCAN (I), 3 mmol; DCA, 0.03 mmol; *trans*-stilbene, 0.6 mmol; acetonitrile, 10 mL; 15 °C.

be seen (Fig. 2). This result confirms the generation of O_2^{-} during photodegradation of this polymer.

The reaction of PCAN with KO_2 was therefore examined to elucidate the mechanism of above photodegradation. 18-Crown-6-ether was used to enhance the solubility of the salt in the solvent used for the reaction. The results are shown in Table 4.

The decrease in the yield of the recovered polymer indicates that decomposition of PCAN occurred during reaction with superoxide anion. In particular, at a higher concentration of superoxide anion the polymer decomposed completely to methanol-soluble products (Table 4, Run 4). The inherent viscosities of the polymers obtained also decreased, and the decrease in the molecular weight of the resulting polymer was accompanied by a decrease in the yield. Prolonged reaction time, however, resulted in no further decreases in the yield or in the inherent viscosity, suggesting that the reaction is rather fast and is completed within 1 hour. These results indicate that the main chain of PCAN was cleaved by reaction with superoxide anion.

$$\mathrm{DCA} \xrightarrow{h\nu} \mathrm{DCA}^{*}$$

$$\mathrm{DCA}^{*} + \mathrm{TS} \longrightarrow \mathrm{DCA}^{\overset{\cdot}{-}} + \mathrm{TS}^{\overset{\cdot}{+}}$$

$$\mathrm{DCA}^{\overset{\cdot}{-}} + O_2 \longrightarrow \mathrm{DCA} + O_2^{\overset{\cdot}{-}}$$

SCHEME 1.

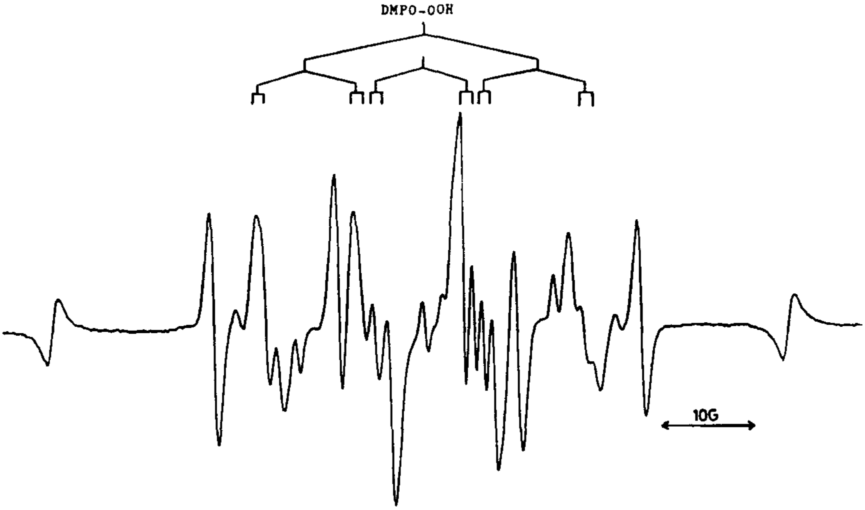


FIG. 2. ESR spectrum of the spin adducts of DMPO obtained by the photoreaction of PCAN in the presence of DCA and TS under oxygen.

Typical IR spectra of the polymers recovered after the reaction are shown for comparison with that of the original PCAN in Fig. 3. The IR spectrum of the resulting polymer in the photoreaction is very similar to that of the polymer obtained in the reaction with superoxide anion. The absorption at 2200 cm^{-1} due to the cyano group of PCAN is quite weak because the chlorine atom on the α-position counteracts the asymmetric stretching vibration of the group [19]. The peak height of this stretching band increased in the IR spectra of the polymers formed during both the photoreaction and the reaction with superoxide anion. These results are indicative of the release of chloride ion from the polymer backbone during the reactions. On the other hand, a new peak appeared at 1720 cm^{-1} after the reactions;

TABLE 4. Reaction of PCAN with KO_2[a]

Run	KO_2, mmol	18-Crown-6-ether, mmol	Yield,[b] %	η_{inh},[c] dL/g
1	0.3	—	83	1.65
2	0.3	0.3	74	1.54
3	0.6	0.3	26	1.10
4	0.9	0.3	0[d]	—[e]

[a] PCAN (III), 3 mmol; DMSO, 10 mL; room temperature, 1 hour.

[b] Precipitated in methanol.

[c] 0.5 g/dL in DMF at 30 °C.

[d] No methanol-insoluble polymer was recovered.

[e] M_n of the methanol-soluble oligomer obtained was 2700.

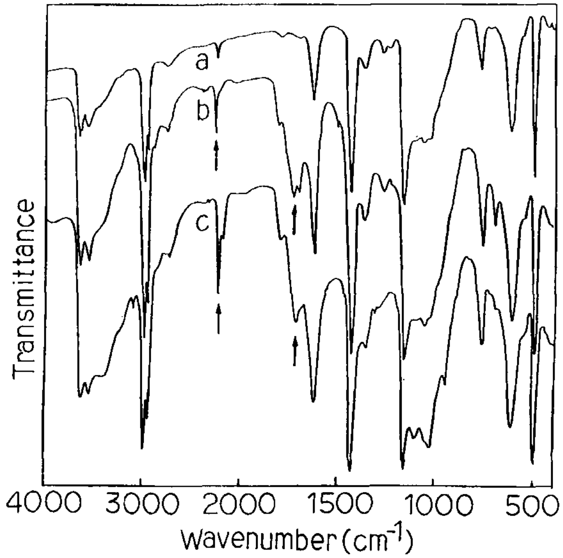


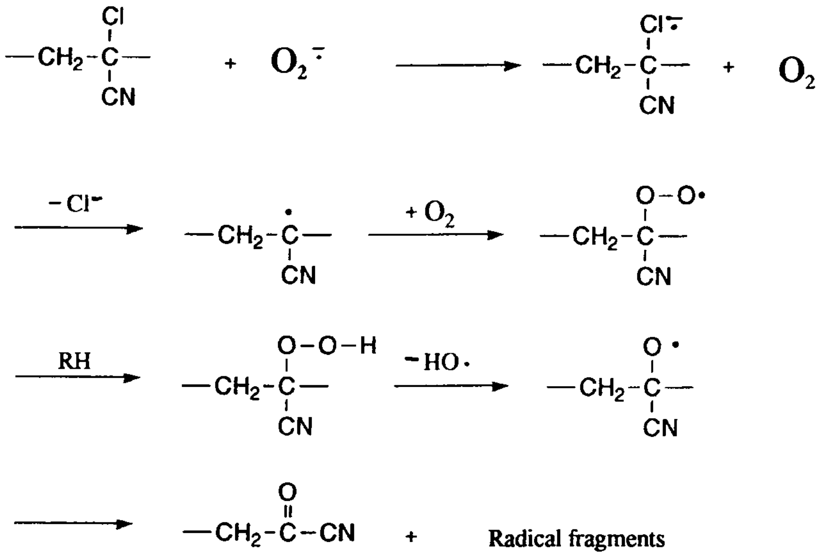
FIG. 3. IR spectra of PCAN (III) before and after the reactions (KBr). (a) PCAN. (b) After the photoreaction (Table 3, No. 3). (c) After the reaction with KO_2 (Table 4, No. 3).

the peak height increased gradually with decreasing inherent viscosities of the recovered polymers. This peak seems to be the absorption of a carbonyl group which may be formed by oxidation, as discussed below.

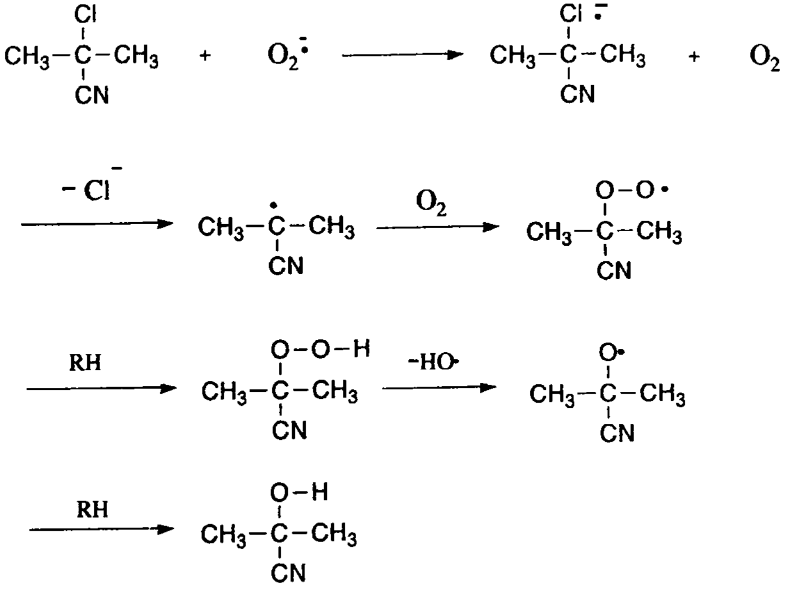
Reaction Mechanism

The results obtained suggest a characteristic photoreaction of PCAN: 1) the main chain of the polymer decomposes as shown by the decrease in the molecular weight; 2) since the IR spectrum of the polymer recovered after the photoreaction is very similar to that of the polymer obtained in the reaction with KO_2, the formation of the superoxide ion causes the degradation of PCAN in the photoreaction; 3) elimination of the chloride ion from the polymer backbone occurs as suggested by the increasing absorption at 2200 cm^{-1} in the IR spectra of the recovered polymers; and 4) the formation of a carbonyl structure in the resulting polymer coincides with scission of the main chain of PCAN because the increase in the IR absorption at 1720 cm^{-1} and the decrease in molecular weight are synchronous. On the basis of these characteristics, a mechanism was deduced for the photodegradation of PCAN (Scheme 2).

First, an electron transfers from the superoxide anion formed as shown in Scheme 1 to PCAN, producing a radical anion on the polymer. Then the chloride anion leaves from the polymer, generating a radical on the backbone which combines with oxygen. The thus formed peroxy radical results in the yield of a carbonyl chain end accompanying scission of the backbone. An analogous formation of peroxy radical has been reported for the reaction of poly(vinyl chloride) with super-



SCHEME 2.



SCHEME 3.

oxide anion [10], and a peroxy radical is known to convert into a carbonyl group [5, 11]. Therefore, the carbonyl groups contained in the resulting polymer are reasonably assumed to form in this manner.

Model Reaction

We examined a model reaction with α-CIBN to confirm the assumed mechanism, in which the reaction with KO_2 produced α-hydroxyisobutylonitrile as the sole product. The assumed mechanism of this reaction is shown in Scheme 3. First, an electron transfers from a superoxide anion to α-CIBN to produce a radical anion, and then the resultant radical anion releases the chloride ion to produce an isobutylonitrile radical. The radical reacts with oxygen, generating a peroxy radical which converts to α-hydroxyisobutylonitrile. The results obtained with this low molecular weight model compound support the mechanism shown in Scheme 2 because, in both cases, the peroxy radical intermediates are formed by substitution of the chlorine for oxygen via an electron transfer as seen in an $S_{RN}1$ reaction. A direct S_N2 reaction of PCAN with $O_2^{\cdot -}$ is unlikely because the chlorine attaches to a tertiary carbon.

CONCLUSION

A remarkable degradation of PCAN was observed in the photoreaction of the polymer under oxygen in the presence of DCA and TS. A similar degradation took place in the reaction of the polymer with KO_2. An ESR measurement using a spin-trapping reagent revealed the generation of $O_2^{\cdot -}$ during the photoreaction of the polymer. On the basis of these results, the mechanism of the photodegradation of the polymer was elucidated as follows: The polymer degrades by the reaction with $O_2^{\cdot -}$ produced by an DCA-mediated electron transfer from TS to oxygen.

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