

SHORT COMMUNICATIONS

**Reductive Decomposition of  $\alpha$ -Brominated Polystyrene Using a Reducing System of Zn–Methylviologen**

Rikiya SATO, Yasushi KOBAYASHI, Yukihito TOMITA,  
Hisashi TAKEUCHI, and Makoto TAKEISHI

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

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The degradation of polymers has attracted much attention primarily because the problem of plastics waste needs to be solved. Many reports on photodegradative and biodegradative polymers have been published. We reported a reductive decomposition of poly( $\alpha$ -chloroacrylonitrile), in which an effective electron transfer from reducing agents to the polymer promotes the reaction.<sup>1</sup> We found that  $\alpha$ -brominated polystyrene (BPSt) decomposes to low molecular weight compounds on the reduction with zinc in the presence of an electron mediation such as methylviologen ( $MV^{2+}$ ). In this communication we report the mechanism of the reductive decomposition of BPSt via the electron transfer from the reducing system of Zn– $MV^{2+}$ .

EXPERIMENTAL

*Materials*

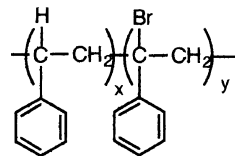
*Preparation of  $MV^{2+}$ .* 1,1'-Dimethyl-4,4'-dipyridinium diiodide (methylviologen diiodide,  $MVI_2$ ) was prepared by the reaction of 4,4'-dipyridyl with methyl iodide in DMF.<sup>2</sup>

*$\alpha$ -Bromination of polystyrene.*<sup>3</sup> BPSt was prepared by the photobromination of commercial polystyrene (Wako Pure Chemical Industries) as follows. A solution of the polymer

(6 mmol) and bromine (6 mmol) in carbon tetrachloride (20 ml) was placed in a Pyrex ampule, which was cooled in liquid nitrogen and sealed under vacuum. The solution in the ample was irradiated with a 400W high pressure mercury lamp at 20°C. The formed BPSt was separated out after precipitation in methanol. The degree of bromination and molecular weights of the polymers are shown in Table I.

*Reaction of BPSt with a Reducing System of Zn– $MV^{2+}$ .* BPSt (1 mmol based on the mono-

Table I. Photochemical  $\alpha$ -bromination of polystyrene<sup>a</sup>



BPSt	Irr. time	x : y <sup>b</sup>	$\bar{M}_n$
	min		
I	1	64 : 36	51000
II	10	44 : 56	36000
III	10	44 : 56	31000
IV	20	24 : 76	41000

<sup>a</sup> Polystyrene  $\bar{M}_n = 60000$ .

<sup>b</sup> Determined by halogen analysis.

mer unit) was dissolved in DMF (2 ml) in a flask,  $MV^{2+}$  (0.2 mmol) was added to the solution, and the flask was purged with nitrogen. After powdered zinc (2 mmol) was added and nitrogen was bubbled into the mixture again, the flask was stoppered and kept in a bath thermostated at 20°C, the contents being stirred with a magnetic bar. The metal powder was filtered out after the reaction and the filtrate was poured into methanol to precipitate the polymer. GPC analysis of the polymers obtained was carried out on a column of polystyrene gel (Shodex A802.5, Shoko Co., Ltd.) using tetrahydrofuran (THF) as the eluent; polystyrene standards were used to calculate  $\bar{M}_n$ .

## RESULTS AND DISCUSSION

Endo *et al.* reported the effective reduction of vicinal dibromides with zinc using viologens as electron-transfer catalysts, in which debromination occurred to produce olefins.<sup>4</sup> The reduction of BPS<sub>t</sub> with this reducing system of Zn- $MV^{2+}$  resulted in decomposition of the polymers as seen Table II (No. 4): all polymer molecules decomposed to low molecular weight

compounds which are soluble in methanol, whereas no degradation of original polystyrene was observed even when both zinc and  $MV^{2+}$  were present.

The reductive decomposition of the polymer is postulated to proceed as shown in Scheme: the electron mediating  $MV^{2+}$  accepts an electron from zinc and the formed  $MV^+$  transfers an electron to BPS<sub>t</sub>, yielding a radical anion of the polymer. Similar reactions are well known as  $S_{RN}1$ ,<sup>4,5</sup> in which single-electron transfer from electron-donating nucleophiles to alkyl halides yields radical anions of the substrates and subsequent release of the halide

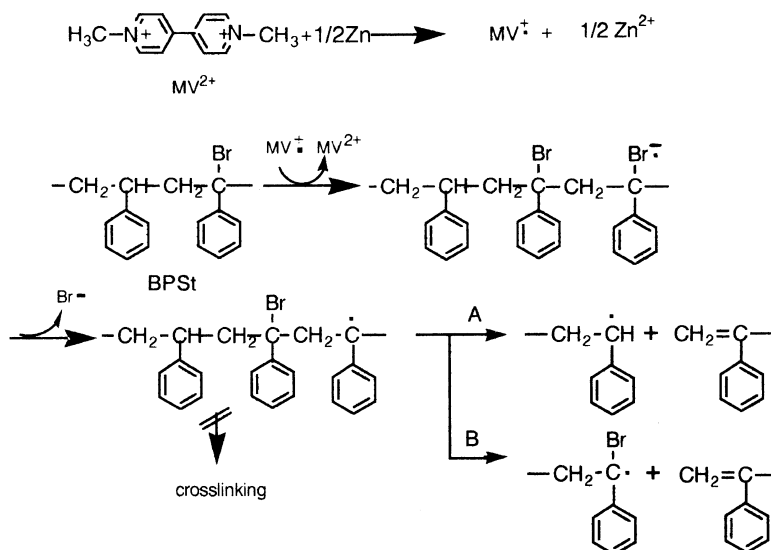
**Table II.** Decomposition of BPS<sub>t</sub>(III) with the reducing system of Zn- $MV^{2+}$ <sup>a</sup>

No.	$MV^{2+}$	Zn	Yield <sup>b</sup>	$\bar{M}_n$
	mmol	mmol	%	
1	—	—	98	30000
2	0.2	—	93	29000
3	—	2.0	93	26000
4	0.2	2.0	trace	500 <sup>c</sup>

<sup>a</sup> Reaction time 1 h.

<sup>b</sup> Precipitated in MeOH.

<sup>c</sup> Methanol-soluble products.

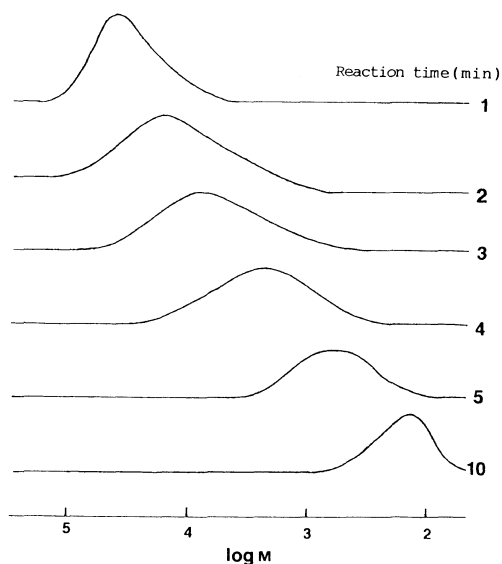


**Scheme 1.**

ion from the substrates generates carbon radicals which couple with the nucleophile anions for propagation of the reaction. In our case, radicals were generated on the polymer chain by leaving bromide ions. A marked decrease in the bromine content of the polymer was observed after the reaction: the bromine content decreased from 36% in starting BPSt(III) to 26% in the recovered polymer after 1 min. The decomposition of polystyrene induced by radicals on the main chain has been reported.<sup>6</sup> Therefore, the generation of radicals on the polymer chain results in scission of the main chain. The scission of type B must be easier than that of type A because of the stabilization of the radical by the bromine atom. Crosslinking by the coupling of the radical on the polymer chain seems unlikely because no gelation of the reaction solution was observed (Scheme 1).

At Table III shows, the molecular weight of the polymer decreased rapidly during the

reaction and almost all polymer molecules decomposed to methanol-soluble low molecular weight oligomers after 3 min.



**Figure 1.** GPC analysis of the BPSt(II) decomposed by reduction. The reaction solutions were injected after zinc was separated out.

**Table III.** Decomposition of BPSt(III) with the reducing system of Zn-MV<sup>2+</sup>

No.	Reaction time	Yield <sup>a</sup>	$\bar{M}_n$
	min	%	
1	1	40	20600
2	2	40	16000
3	3	trace	2600 <sup>b</sup>
4	5	trace	1500 <sup>b</sup>

<sup>a</sup> Precipitated in methanol.

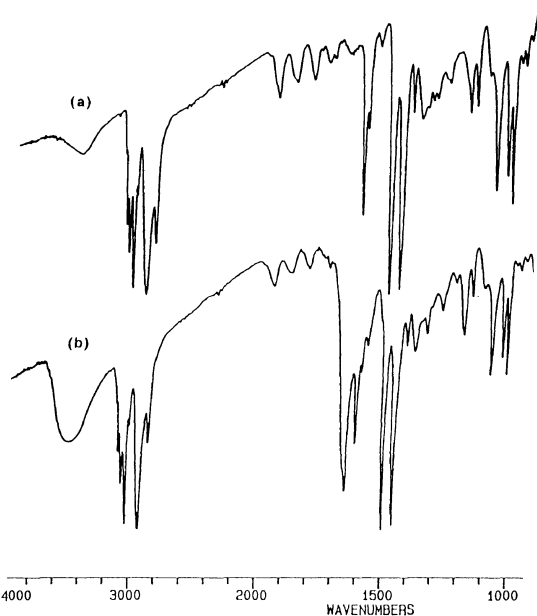
<sup>b</sup> Methanol soluble products.

**Table IV.** Effects of bromine content on the reductive decomposition of BPSt<sup>a</sup>

BPSt	$\alpha$ -Bromination	Yield	$\bar{M}_n$
	%	%	
I	36	40	31000
III	56	trace	2600 <sup>b</sup>
IV	76	trace	1500 <sup>b</sup>

<sup>a</sup> Reaction time 3 min.

<sup>b</sup> Methanol-soluble products.



**Figure 2.** IR spectra of BPSt(II) before and after the reaction for 3 min (KBr). (a) before the reaction; (b) after reaction with the reducing system Zn-MV<sup>2+</sup>.

The rate of the reductive decomposition of BPSt depends directly on bromine content as shown in Table IV. The molecular weights of the polymers recovered decreased with increasing bromine content. BPSt with degree of  $\alpha$ -bromination of monomer unit above 56% decomposed to methanol soluble oligomers.

Change in the molecular weight of the polymer during the reaction is shown in Figure 1. After reaction for 10 min, most polymers decomposed to methanol soluble compounds ( $\bar{M}_n = 500$ ).

The IR spectra of the polymer before and after reductive decomposition are shown in Figure 2, in which a new absorption peak at  $1640\text{ cm}^{-1}$  developed after the reaction. This peak was due to carbon-carbon double bonds formed by the chain scission in Scheme 1.

The above reductive decomposition proceeded in the dark. Photochemical electron transfer to halogenated polymers interested us

because such a photo-induced system will give new prospects for the production of photodegradative polymeric materials. Some photo-reactions are now under investigation.

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