

NOTES

Photodegradation of Brominated Polystyrene

INTRODUCTION

Degradation of polystyrene has been widely studied. Its initial step is understood to be triggered by the abstraction of hydrogen from the α -carbon of the styrene unit and the formation of free radicals. When polystyrene is heated in chlorobenzene with azobisisobutyronitrile, for example, the degradation is accelerated by the formation of peroxide to the α -carbon.¹ The bond between carbon and halogen is liable to suffer photochemical scission. With increase in the atomic number of the halogen, the wavelength of the light absorbable by the compound becomes longer and the dissociation energy of the C-X bond becomes smaller. Photodegradation of brominated polystyrene, C-Br being the heaviest combination that does not absorb visible light, was examined with this understanding.

EXPERIMENTAL

Polystyrene, $\bar{M}_n = 1.9 \times 10^5$, obtained by anionic polymerization with sodium naphthalene initiator, was brominated according to Jones's method² using a 500-W xenon lamp (Ushio Electric Co.) and a filter to cut off the light below 410 $m\mu$. For photodegradation, a dilute solution (1 g polymer in 60 ml solvent) was irradiated in a 60-ml three-necked quartz flask to induce the scission of main chains without crosslinking. Molecular weight of the polymer was measured in toluene at 37°C using a Hewlett-Packard 501 high-speed membrane osmometer. ESR spectra were measured with a JES 3BSX spectrophotometer of Japan Electron Optics Lab. Wavelength of the microwave was around 9400 megacycle.

RESULTS AND DISCUSSION

The conditions and results of the photobromination of polystyrene are summarized in Table I. Addition of bromine to polystyrene was 50–80% of theoretical, even though the color of bromine had completely disappeared at the end of the reaction. A decrease in molecular weight was observed in the photobromination. Brominated polystyrene is a white powder; the brominated position is considered to be mainly the most reactive α -hydrogen of the styrene unit. The spectrum of the brominated polystyrene in Figure 1 demonstrates that the absorption at 280–360 $m\mu$ increased very much compared with the original absorption. The brominated polystyrene is yellowish when it is dissolved in solvents.

TABLE I
Photobromination of Polystyrene

PSBr No.	Conditions of bromination					Properties of PSBr	
	PS, g	CCl ₄ , ml	Br ₂ , ml	Time, min	Atmosphere	Br-content (wt%)	$\bar{M}_n \times 10^{-4}$
4	6	200	0.4	11	air	5.40	5.6
6	20	400	0.5	7	ar	3.04	13
7	20	400	0.5	8	air	2.39	12

TABLE II
Effect of Solvent and Atmosphere*

Solvent	$\bar{M}_n \times 10^{-4}$	
	In air	In Ar
Carbon tetrachloride	4.1	8.7
Benzene	4.0	5.9
Ethyl acetate	6.7	6.8
Benzyl chloride	6.1	5.9
Ethylbenzene	8.3	10

* PSBr no. 6; irradiation time 45 min.

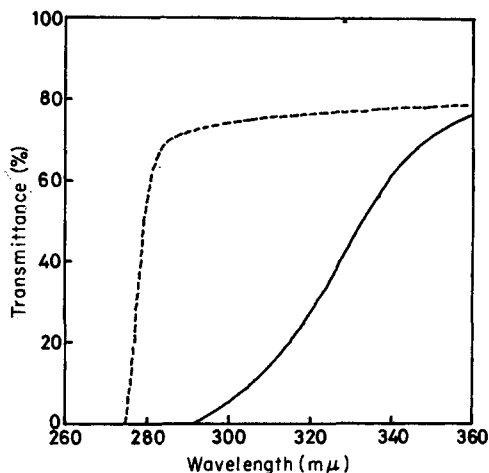


Fig. 1. Absorption spectra of brominated polystyrene: Abscissa, wavelength ($m\mu$); ordinate, transmittance (%); (—) brominated polystyrene (PSBr no. 4); (---) polystyrene.

Table II shows the effects of atmosphere and solvents on the photodegradation. Molecular weights of the brominated polystyrene irradiated in carbon tetrachloride, benzene, and ethyl benzene were smaller in air than in argon atmosphere. In these solvents, a decrease in molecular weight is regarded as being promoted by the degradation through peroxide formation. In ethyl acetate and benzyl chloride, no atmospheric effect was observed. In ethylbenzene that carries abstractable hydrogen, the molecular weight decrease was smaller than in benzene. The chlorine atom of benzyl chloride is also easily abstracted. In fact, the chain transfer constant of the polystyryl radical is larger in benzyl chloride than in ethylbenzene.³ The decrease in molecular weight is, however, smaller in benzyl chloride than in ethylbenzene, probably because of the characteristics of chlorine and hydrogen. When benzyl chloride is compared with carbon tetrachloride, the abstractable atom of which is also chlorine, the decrease in molecular weight in argon atmosphere is smaller in carbon tetrachloride by reason of its higher chain-transfer constant.

Figure 2 shows the relationship between molecular weight and irradiation time. Whereas the original polystyrene was stable to irradiation, the molecular weight of brominated polystyrene decreased with irradiation time—it dropped rapidly at the beginning, then kept the same value after 30 min and did not decrease below 3×10^4 . Since the brominated polystyrene contains an average of 36 atoms of bromine in a mole-

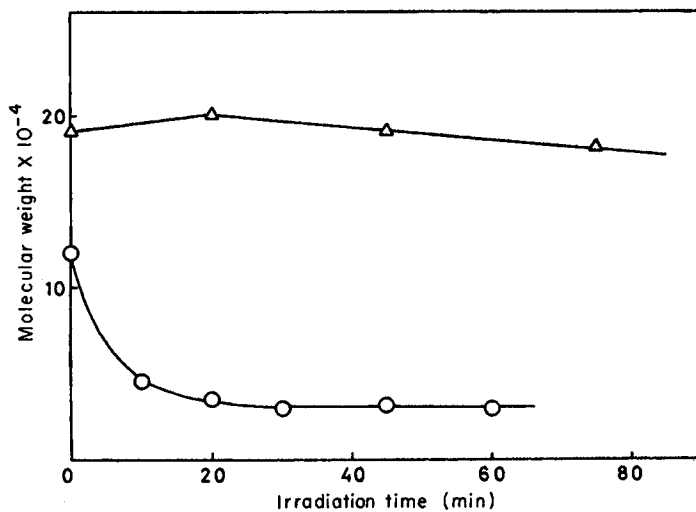


Fig. 2. Dependence of molecular weight on irradiation time: (—○—) PSBr no. 7; (—△—) polystyrene; solvent, benzene; abscissa, irradiation time (min); ordinate, molecular weight $\times 10^{-4}$.

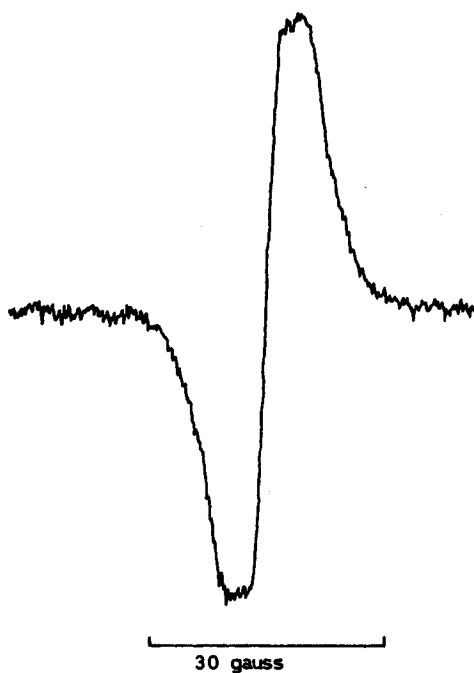


Fig. 3. ESR spectrum of brominated polystyrene: PSBr no. 4; 29% benzene solution; irradiation, 4 hr.

cule, the molecular weight should decrease to 3.2×10^8 if the degradation proceeded completely. The actual number of scissions is calculated to be three in a molecule, and the efficiency of the main-chain scission is 8% per bromine atom.

Irradiation of the brominated polystyrene is considered to induce free radicals by the abstraction of bromine. The existence of free radicals has been ascertained by a singlet ESR spectrum in Figure 3. The produced radicals diminished but still remained observable 20 hr after the cessation of irradiation. It has been reported that γ -ray irradiation to polystyrene induces the abstraction of α -hydrogen and gives a spectrum consisting of three peaks with a separation of 37 gauss between center and end derivative peaks.⁴ The fact that the observed spectrum of the irradiated brominated polystyrene was such a sharp singlet is explained by the formation of polyenyl-type radicals induced by the abstraction of hydrogen which succeeded to the abstraction of bromine. The existence of a polyenyl-type radical is also responsible for the low efficiency of main-chain scission. Irradiation of brominated polystyrene is concluded to produce main-chain scission and polyene formation after the abstraction of bromine.

Irradiation of poly(vinyl chloride) induces dehydrochlorination. Even in poly(vinyl chloride)-carbon monoxide copolymers, no change was observed in molecular weight after irradiation.⁵ The notable decrease in molecular weight observed in brominated polystyrene may be partly due to the difference between bromine and chlorine. But the main reason is the difference between hydrogen and the phenyl group and the distribution of halogen atoms. These findings, along with other reports, will contribute to the promotion of photodegradation of vinyl polymers and to the elucidation of degradation mechanisms.

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References

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