

*Reaction of SO<sub>2</sub> with Polymer*

A survey of the effect of NO<sub>2</sub> and SO<sub>2</sub>, respectively, on various polymers was presented recently.<sup>1</sup> This note gives some additional data on the deterioration of polymers by SO<sub>2</sub>, particularly in the presence of near-ultraviolet light ( $\lambda > 2800 \text{ \AA}$ ) and oxygen.

The apparatus, light source, and exposure procedure to ultraviolet light were the same as described previously.<sup>1</sup> The purification of the polymers was effected by pouring a 1%-2% w/v solution into an excess of nonsolvent at 25°-30°C. Isotactic polystyrene, isotactic poly(methylmethacrylate), and poly- $\alpha$ -methylstyrene were precipitated by methanol from benzene solutions. Polyvinylpyrrolidone (K90) and polyvinylformal were precipitated from chloroform solutions by hexane and polycarbonate was precipitated from methylene chloride solution by methanol.

The preparation of the films (ca. 25 $\mu$  thick) by casting on mercury or aluminum foil surfaces, respectively, was described previously. The films were dried thoroughly and finally placed into a high vacuum apparatus for 24 hr at 40°C. The results are given in Table I below.

TABLE I  
Summary of Experimental Results<sup>a</sup>

Exposure Conditions	[ $\eta$ ], dl/g					
	ISO-PSTY	ISO-PMMA	P- $\alpha$ -MSTY	PVP	PVF	PC
Before Exposure	2.32	2.55	1.32	2.22	1.32	0.50
SO <sub>2</sub> (1 cm Hg)	2.39	2.56	1.38	2.27	1.37	0.50
Dark						
SO <sub>2</sub> (1 cm Hg)						
Air (1 atm)	2.36	2.50	1.36	2.27	1.48	0.49
Dark						
UV	2.40	2.63	1.35	2.10	1.43	0.53
Vacuum (10 <sup>-5</sup> mm Hg)						
UV				43%		
O <sub>2</sub> (15 cm)	2.32	2.56	1.38	crosslinked	1.38	0.46
UV				8.5%		
O <sub>2</sub> (15 cm Hg)	1.02	1.13	0.79	crosslinked	0.97	0.50
SO <sub>2</sub> (1 cm Hg)						

<sup>a</sup> Exposure, 10 hr at 25°C;  $\lambda > 2800 \text{ \AA}$ .

Isotactic polystyrene and isotactic poly(methyl methacrylate) deteriorate less than the atactic isomers, except when exposed to a combination of UV, O<sub>2</sub>, and SO<sub>2</sub>. In the latter case more chain scission takes place in the isotactic polymers than in the atactic ones. The decrease in [ $\eta$ ] is 17% and 55%, 29% and 55% for atactic and isotactic polystyrene and polymethylmethacrylate, respectively.

Poly- $\alpha$ -methylstyrene shows a pronounced decrease in [ $\eta$ ] (ca. 40%) when exposed to the combination of UV-O<sub>2</sub>-SO<sub>2</sub>. It is appreciably more reactive than atactic polystyrene. However, it withstands any of the other conditions indicated in Table I. Polyvinylpyrrolidone is extensively crosslinked while exposed to UV-O<sub>2</sub> and less so in the presence of UV-O<sub>2</sub>-SO<sub>2</sub>. The photolysis in aqueous solution in the absence and presence of oxygen was investigated recently.<sup>2</sup>

Polyvinylformal shows a decrease in [ $\eta$ ] of about 27% when exposed to UV-O<sub>2</sub>-SO<sub>2</sub>. Crosslinking appears to take place under all other conditions, especially in SO<sub>2</sub>-air in the

dark. Polycarbonate practically does not show any effect under all of the conditions of exposure. There is an indication of very slight chain scission when it is exposed to UV-O<sub>2</sub>.

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### References

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H. H. G. Jellinek  
F. J. Kryman

Department of Chemistry  
Clarkson College of Technology  
Potsdam, New York 13676

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