

Reaction of SO₂ and NO₂ with Polymers

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Synopsis

A number of polymers have been exposed to SO₂ and NO₂ gas under various conditions. Chain scission, crosslinking reactions, and changes in infrared spectra have been noted. All polymers suffer some deterioration, which may be considerable with exposure over long periods of time. Elastomers form a separate group, being appreciably more susceptible to these gases than saturated polymers; however, they are still more sensitive to ozone.

Scarcely any work has been done on reactions of gases (air pollutants), such as SO₂ and NO₂ with polymers. A beginning has been made recently by Jellinek and Toyoshima, who studied the reaction of NO₂ with polystyrene.¹ Some work has also been carried out on the reaction of NO₂ with polyethylene by Ogihara et al.^{2,3} who followed changes in infrared spectra. More recently, Bruksch⁴ surveyed infrared spectra of various polymers as function of exposure to ozone, sulfur dioxide, various acids, oxygen, and ultraviolet light.

The present survey is concerned with the effect of SO₂ and NO₂ alone, in the presence of oxygen, and in additional presence of ultraviolet light from the standpoint of chain scissioning and crosslinking. This survey also include elastomers, which, with respect to these reactions, form a class in themselves.

EXPERIMENTAL

Exposure to Sulfur Dioxide Gas

Apparatus. An all-glass, high-vacuum system was used for the reactions. An assembly of six Pyrex reaction tubes surrounded the ultraviolet light source, (Hanovia, high-pressure mercury lamp, 654A-36). The lamp was stabilized by a constant-voltage transformer, and the whole arrangement was submerged in a water thermostat. SO₂ gas was obtained from Matheson Company, Inc. (anhydrous grade, SO₂ 99.98% minimum; moisture 50 ppm, non-volatiles 30 ppm maximum, acidity as H₂SO₄ 10 ppm maximum).

The SO₂ gas was passed through drying towers and glass wool into the vacuum system. The vacuum was of the order of 10⁻⁵ mm Hg. All wavelengths below 280 m μ were removed by Pyrex glass, No. 7740.

Purification of Polymers. Each polymer was purified by pouring a 1-2% (w/v) solution into excess nonsolvent. Table I gives the polymers, their origin, the solvents, the nonsolvents, and the temperature at which the precipitation was carried out.

TABLE I
Purification of Polymers by Precipitation

Polymer	Solvent	Precipitant	Precipitation temperature, °C
Polystyrene B9, isothermal, Dow Chemical Company	Methyl ethyl ketone	Methanol	25
Polyethylene (low density, Dow Chemical Company)	Toluene (100°C)	Toluene (25°C)	25-100
Polypropylene (XPRD-A1115), Polymer Corp., Sarnia, Canada)	Toluene (100°C)	Toluene (25°C)	25-100
Polybutadiene (Budene, Goodyear, Akron)	Benzene	Methanol	25
Butyl rubber (XPRD-124A, 99.2% isobutylene 0.8% isoprene, Enjay Chemical Corporation)	Benzene	Methanol	25
Polyisoprene (Natsyn, Goodyear)	Benzene	Methanol	25
Poly(methyl methacrylate) (Eastman Organic Chemicals)	Acetone	Methanol	25
Poly(vinyl chloride) (Opalon 330, Chemstrand Corporation)	Cyclohexanone	Methanol	25
Polyacrylonitrile (Chemstrand Corporation)	Dimethylformamide	Water	25
Nylon 66 (Chemstrand Corporation)	97% Formic acid	Methanol	25

Film Preparation. Polymer films were cast from solution (ca. 6% w/v) onto flat surfaces. The volume of the solution controlled the film thickness (ca. 20-30 μ). The solvents and drying conditions are given in Table II for the experiments with SO₂. The solvents for each polymer were the same as those used for purification, except for poly(methyl methacrylate) and poly(vinyl chloride), where benzene and tetrahydrofuran were used, respectively.

Procedure for Exposure of Polymers. Films of each of the polymers were exposed to a total of five different conditions at 25°C. Infrared spectra, where possible, were also taken before and after exposure. The films were dissolved after exposure and intrinsic viscosities were determined in

Cannon-Fenske viscometers at 25°C. The amount of crosslinking was determined, whenever it occurred.

Films were mounted in separate reaction vessels. The apparatus was evacuated to at least 10⁻⁵ mm Hg for 12 hr before gases were introduced. The exposure conditions are given in Table IV below. For the dark reactions, light was excluded by wrapping aluminum foil around the reaction vessels. The films had to be degassed after exposure in order to remove all residual gas, thus preventing further reaction. Intrinsic viscosities were determined under the conditions indicated in Table III.

The results of the intrinsic viscosity determinations are given in Table IVA. Per cent crosslinking is indicated by % CL in the same table.

TABLE II
Conditions for Film Casting and Drying

Polymer	Casting	Drying
Polyethylene (PE)	Solution 85°C, solvent evaporated at 100°C in air	High vacuum (10 ⁻⁴ mm Hg) 50°C, 48 hr
Polypropylene (PPRO)	Solution 100°C, solvent evaporated at 115°C in air	High vacuum, 25°C, 24 hr
Polystyrene (PSt)	Solution 25°C, solvent evaporated at 25°C in air	High vacuum
Poly(methyl methacrylate) (PMMA)		40°C, 24 hr
Poly(vinyl chloride) (PVC)	Solution 25°C, solvent evaporated in vacuum oven at 45-50°C	High vacuum
Polyacrylonitrile (PAN)		40°C, 24 hr
Nylon	Solution 25°C, solvent evaporated in vacuum oven at 45-50°C	High vacuum 40°C, 24 hr
Polybutadiene (PBD)	Solution 25°C, solvent evaporated at 24°C under nitrogen	High vacuum,
Butyl rubber (BUR)		40°C, 24 hr
Polyisoprene (PISO)		

TABLE III
Conditions for Viscosity Determination

Polymer	Solvent	Temperature, °C	Atmosphere
Polyethylene	<i>p</i> -Xylene	81	N ₂
Polypropylene	<i>p</i> -Xylene	84	N ₂
Polystyrene	Benzene	25	Air
Poly(methyl methacrylate)	Benzene	25	Air
Polyacrylonitrile	Dimethylformamide	25	Air
Poly(vinyl chloride)	Tetrahydrofuran	20	Air
Nylon	Formic acid 97%	25	Air
Butyl rubber	Benzene	25	N ₂
Polyisoprene	Benzene	25	N ₂
Polybutadiene	Benzene	25	N ₂

TABLE IVA
Summary of Experimental Results on Exposure to SO₂ (25°C)

PE (10 hr)	PPRO (10 hr)	PST (10 hr)	PMMA (10 hr)	PVC (10 hr)	PAN (10 hr)	Nylon (5 min)	BUR (5 min)	PISO (5 min)	PBD (5 min)
[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g
0.82	2.10	1.23	1.18	1.00	0.59	2.40	0.66	3.40	2.80
0.8	2.15	1.20	1.16	0.93	0.45	3.06	0.64	3.64	7 μ
0.81	2.21	1.33	1.19	0.96	0.59	2.68	0.65	3.57	32
1.00	2.19	1.21	1.17	0.98	0.79	2.37	0.66	3.28	18
1.03	2.10	1.14	1.10	0.97	0.50	2.35	0.64	3.03	53
—	100	69	1.02	0.95	0.48	2.47	0.59	3.15	52

Before exposure, dark
 SO₂ (1 cm Hg), dark
 SO₂ (1 cm Hg), air (1 atm),
 dark
 UV, vacuum (10⁻³ mm Hg)
 UV, O₂ (15 cm Hg)
 UV, O₂ (15 cm Hg), SO₂
 (1 cm Hg)

TABLE IVB
Summary of Experimental Results on Exposure to NO₂ (35°C)

PE (30 hr)	PPRO (30 hr)	PST (30 hr)	PMMA (30 hr)	PVC (30 hr)	PAN (30 hr)	Nylon (1/2 hr)	BUR (1/2 hr)	PISO (5 min)	PBD (5 min)
[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g	[η], dl/g
CL	CL	CL	CL	CL	CL	CL	CL	CL	CL
%	%	%	%	%	%	%	%	%	%
0.91	2.10	0.96	1.16	0.94	0.82	1.36	0.65	3.44	2.73
0.92	1.77	0.83	1.06	0.80	0.82	1.17 ^a	0.62 ^a	1.41 ^a	53.5 ^a
0.92	1.92	0.83	1.08	0.88	0.82	0.59 ^a	0.51 ^a	0.48 ^a	61 ^{a,b}
0.92	1.87	0.96	1.07	0.94	0.85	1.36 ^a	0.64 ^a	3.06 ^a	2.58 ^a
0.96	1.94	2.6	1.11	0.89	0.85	1.34 ^a	0.65 ^a	2.94 ^a	2.73 ^a
0.95	1.83	4.7	1.0	0.88	0.81	0.82 ^a	0.61	0.46 ^a	39.4 ^a

^a These values for NO₂ pressure of 1 cm Hg.

^b % CL at 7 min = 76.

Exposure to Nitrogen Dioxide Gas

There are some differences in experimental detail in the case of NO₂ from those used for sulfur dioxide.

Apparatus. The high vacuum apparatus was in principle similar to that used for SO₂. The lamp and reaction vessels were somewhat differently arranged. The ultraviolet lamp was a G.E. high-pressure mercury lamp, 250 UA-2, which had to be water-cooled. Its maximum output was in the region of 3600–3700 Å. A Corning filter CS 7-39, Pyrex NO. 5874, which had its maximum transmission (ca. 55%) at 3600 Å (band width 3000–4000 Å) was used. The conditions of exposure are given in Table IVB. The NO₂ gas (Matheson) contained not more than 20 ppm of NOCl, expressed in chloride, water equivalent 0.6%, particulate 1.0 mg/l.

Procedure. The film drying procedure for polyethylene, polypropylene, poly(methyl methacrylate), poly(vinyl chloride), and nylon consisted of preliminary drying in a vacuum oven at 40°C, followed by drying for 20 hr under a vacuum of 0.05 mm Hg at 40–50°C, following by evacuating to 10⁻⁵ mm Hg in the vacuum assembly before gases were introduced. NO₂ and O₂ were not especially dried before use. Polystyrene was ultimately dried for 40 hr at 50°C in high vacuum (10⁻⁵ mm Hg) before exposure. Also polyacrylonitrile was dried for 20 hr in high vacuum prior to exposure. The three elastomers were first dried under N₂ at room temperature and subsequently, under a vacuum of 0.025 mm Hg before exposure.

The casting conditions were the same as described under sulfur dioxide, except for PVC, which was cast from cyclohexanone solution. Viscosity measurements were similar as described before, except the solvent for polystyrene was dioxane at 3–5°C. The percentage formic acid used for dissolving nylon (90%) was somewhat different from that used before for SO₂ (97%).

The exposure conditions in the case of nitrogen dioxide were somewhat more drastic than those in the case of sulfur dioxide. All exposures were carried out at 34°C and not 25°C as was the case with SO₂. All films exposed to NO₂ had a yellowish color; the elastomer and nylon films were of such a consistency that infrared spectra could not be taken.

Infrared Spectra

Infrared spectra were taken before and after exposure of all polymer films except those for nylon and the elastomers. The following observations were made.

SO₂ Exposure. For polyethylene the absorption at 7.3 μ decreased on exposure to UV-O₂-SO₂, and the sample was practically completely cross-linked. With poly(vinyl chloride), on exposure to UV-O-SO₂, a carbonyl band appeared at 6.9 μ and the extinction around 10 μ decreased, indicating a loss of Cl.

Polyacrylonitrile showed a peak of residual dimethylformamide at 6.1 μ, whose amount is not more than 1% w/v. This was determined by

known amounts of solvent in the film. Molar absorptivity of the solvent was approximately 4×10^3 .

NO₂ Exposure. Polyethylene showed a new band at 6.4μ on exposure to NO₂ (15 cm Hg). This is due to nitro groups along the backbone of the polymer.

Poly(methyl methacrylate) shows some changes at 2.8μ when exposed to 15 cm NO₂, which are less pronounced when exposed to 1 cm NO₂-O₂-UV.

Polyacrylonitrile shows a band due to residual dimethylformamide at 5.95μ . There are some changes in the spectrum at 11.5μ . (Residual solvent is less than 1% w/v.)

Poly(vinyl chloride) shows the C=O band of residual cyclohexanone (5.85μ), which was used as solvent (maximum 12% w/v, molar absorptivity ca. 1.4×10^2). The C-Cl band disappeared, when exposed to NO₂ alone, but did not vanish completely when exposed to UV-O₂-NO₂. A band at 6.4μ appears on exposure under all conditions when NO₂ is present. This is due to formation of NO₂ side groups incorporated along the backbone of the polymer.

DISCUSSION

It is known that SO₂ reacts on irradiation with ultraviolet of light wavelength $> 3000 \text{ \AA}$ as follows,



In the presence of oxygen, ozone can be formed³



The photochemical reaction of SO₂ with saturated and unsaturated hydrocarbons was studied by Dainton and Ivin.⁵ Sulfinic acids are formed and the 120° angle of SO₂ is straightened out,



The proposed mechanism for the photo-reaction of SO₂ with saturated hydrocarbons is as follows,



An unsaturated hydrocarbon supposedly reacts as follows, where B is unsaturated hydrocarbon.





Thus, SO_2 will be effective and so will ozone.

Nitrogen dioxide is always present in equilibrium with the dimer,



NO_2 is the reactive species as it is an odd-electron molecule. The total gas pressure, if only nitrogen dioxide and the dimer are present, is given by,

$$P_{\text{total}} = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} \quad (11)$$

Further,

$$K_p = P_{\text{NO}_2}^2 / P_{\text{N}_2\text{O}_4} \quad (12)$$

which, combined with eq (11) gives,

$$K_p P_{\text{total}} = P_{\text{NO}_2}^2 + K_p P_{\text{NO}_2}$$

The partial pressure of NO_2 in the system is then,

$$P_{\text{NO}_2} = [-K_p + (K_p^2 + 4K_p P_{\text{total}})^{1/2}] / 2 \quad (13)$$

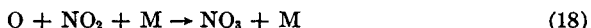
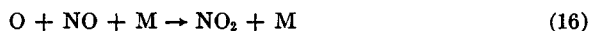
for example for 35°C , one obtains, for $P_{\text{total}} = 15$ cm Hg, $K_p = 0.315$ cm Hg, $P_{\text{NO}_2} = 10.4$ cm Hg; for $P_{\text{total}} = 30$ cm Hg, $K_p = 0.30$ cm Hg, $P_{\text{NO}_2} = 17.4$ cm Hg; for $P_{\text{total}} = 60$ cm Hg, $K_p = 0.272$ cm Hg, $P_{\text{NO}_2} = 26.35$ cm Hg.

Nitrogen dioxide reacts with suitable hydrocarbons by removing, preferentially, a tertiary hydrogen atom,¹



The radical $\text{R}\cdot$ then reacts with NO_2 leading either to nitro or nitrite side groups along the polymer backbone or to chain scission and/or crosslinking. A chain reaction ensues, which has similarities with the oxidative chain reactions for hydrocarbons.⁶

In the presence of near ultraviolet light, the reactions (15)–(21) take place:⁷



Reactions (20) and (21) are fast.

Polyethylene on exposure to SO_2 alone and in presence of air does not show any change during the time of exposure. However, on irradiation

with ultraviolet light in absence and presence of oxygen, there are indications of an increase in viscosity. This may simply be due to severance of branches at the tertiary carbon atoms, which would cause an increase in intrinsic viscosity. When this polymer is exposed to UV-O₂-SO₂, it practically completely crosslinks. In contrast to this behavior, NO₂ has no effect, except for some indication of a slight increase in viscosity in presence of UV-O₂ and UV-O₂-NO₂. The infrared spectrum indicates incorporation of nitro groups into the polymer backbone (6.4 μ).

Polypropylene is not affected except in the system UV-O₂-SO₂, where large amounts of crosslinking take place. Whether the ozone produced in presence of ultraviolet light is responsible for this crosslinking of propylene and also of polyethylene is not known. The amount of crosslinking is much smaller in the presence of UV-O₂-NO₂. There are indications that some chain scission takes place under all of the other conditions.

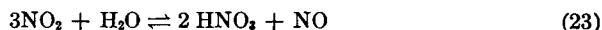
Polystyrene is scarcely affected by either SO₂ or NO₂ under the experimental conditions. There are indications of some chain scissioning in the presence of NO₂. Polystyrene has been investigated in some detail by Jellinek and co-workers.⁶

Poly(methyl methacrylate) is not affected by SO₂ except for some chain scissioning in the presence of UV-O₂ and UV-O₂-SO₂. Some chain scission takes place in the absence and presence of ultraviolet light with and without oxygen and NO₂. The infrared spectrum indicates some change at 2.8 μ (OH group) in the presence of NO₂ alone.

Poly(vinyl chloride) shows very little change in as far as the intrinsic viscosity is concerned, but shows loss of chlorine (ca. 13 μ) in the presence of either SO₂ or NO₂. In the presence of NO₂, the band at 7.5 μ disappears (probably ~HC(Cl)—CH stretching band).

Polyacrylonitrile does not show anything significant in the presence of SO₂ or NO₂. There is some change in the infrared spectrum at 11.4 μ.

Nylon, being a condensation polymer, represents a special case. SO₂ seems to lead to some crosslinking, which is less pronounced in the presence of oxygen and ultraviolet radiation. However, in the presence of NO₂, chain scission takes place, which is quite pronounced in the additional presence of air. Chain scissioning takes place also in UV-O₂-NO₂. This reaction is probably a hydrolysis reaction due to the presence of moisture. NO₂ may react with water in the dark as shown by eq. (22) and (23):



In ultraviolet light, there are a number of possibilities for producing acids.

The elastomers (unsaturated polymers) form a class in themselves. They are much more susceptible to NO₂ and SO₂ than the saturated polymers. Whether the main effect is due to ozone generated during several relevant reactions is not yet known. However, this is not unlikely as the following data for polymers exposed to O₃ in the form of films show: Polystyrene film exposed to 0.6 ppm of O₃ in air: before exposure $[\eta]$ 4.16 dl/g,

after exposure for about 30 hr $[\eta] = 4.09$ dl/g; butyl rubber (0.8% unsaturation) before exposure $[\eta] = 0.715$ dl/g, after exposure to 0.016 ppm O_3 , $[\eta] = 0.697$ dl/g, 0.018 ppm O_3 $[\eta] = 0.702$ dl/g.

Butyl rubber is fairly stable when exposed for 5 min to SO_2 or SO_2-O_2-UV , an indication of occurrence chain scissioning for the latter condition. Similarly, NO_2 does not produce much change during 30 min exposure. Here again some chain scissioning is indicated, especially in the presence of NO_2 and air.

Polyisoprene shows some signs of crosslinking, when exposed 5 min to SO_2 and SO_2 plus air in the dark; in the presence of $UV-O_2$ and $UV-O_2-NO_2$, there are indications of chain scissioning. With NO_2 alone, chain scissioning takes place, which becomes very appreciable if oxygen is also present; also a slight amount of crosslinking is found. The strongest chain-scission effect occurs in presence of $UV-O_2-NO_2$.

Polybutadiene is affected under all conditions, in absence and presence of SO_2 ; crosslinking takes place in all cases, especially in the presence of SO_2 in the dark and in the presence of $UV-O_2$ and $UV-O_2-SO_2$. Crosslinking also takes place in the presence of NO_2 alone, NO_2 plus air and $UV-O_2-NO_2$, but not with ultraviolet light alone or in presence of ultraviolet and oxygen.

There is no doubt that the damage caused by SO_2 and NO_2 to the elastomers will be quite extensive, although probably not quite as drastic as that caused by ozone alone.

As far as the unsaturated polymers are concerned, they are much more resistant than the elastomers, but also they will suffer considerably damage when exposed over long periods of time, even at small gas concentrations.

Moreover, chain scission and crosslinking are not the only criteria of deterioration; reactions of side groups, mechanical, electrical, and optical properties have also to be considered.

In addition, in reality, a number of gases, not only one, is present at any one time. There may be synergistic effects, about which there is no knowledge at present, except for work on low-molecular hydrocarbons.

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