BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (5), 1487—1489 (1978)

The Role of the Charge-transfer Complex in the Photocopolymerization of Oxygen with Styrene and α-Methylstyrene

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(Received October 25, 1977)

The effect of the wavelength of irradiated light on the photocopolymerizations of oxygen with styrene (**1**) and α-methylstyrene (**2**) was investigated in connection with the charge-transfer bands observed between these monomers and oxygen, with the latter as an electron acceptor. It appeared that the excitation of the charge-transfer bands is responsible for the copolymerizations and that the photoabsorptions due to **1** and **2** do not contribute to the reactions, although the excited singlet states of these compounds were quenched by oxygen according to a Stern-Volmer plot.

The bathochromic shifts of the electronic absorption bands of several monomers including styrene (**1**) and α-methylstyrene (**2**) were observed while the electronic spectra were measured for these compounds saturated with oxygen.[1] The extra absorption bands were attributed to contact charge-transfer (CT) complexes between them and oxygen, with the latter as an electron acceptor, by taking into consideration the similar absorptions observed for various organic substances.[2] The photopolymerization of **1** in the presence of oxygen revealed that the CT-band plays an important role as a light-absorbing species in the formation of the alternating copolymer of **1** with oxygen.[1] Some contribution from the exciplex between oxygen and the excited singlet **1** to the formation of the alternating copolymer was also suggested based upon the measurements of the fluorescence spectra of **1** in the presence of oxygen under various pressures, but no detailed polymerization data were reported in connection with the excitation of **1**.[1] For this reason, the effect of the wavelength of irradiated light on the photocopolymerization of **1** with oxygen has been investigated to get further information on the contribution from the excited singlet **1** to the copolymerization. During the course of this study, it appeared that **2** also yields an alternating copolymer, with oxygen as a comonomer, on the excitation of **2** in the region of the CT-band. Therefore, similar experiments have also been carried out for **2**. Photo- and thermal-copolymerizations of these compounds by using azobisisobutyronitrile have already been reported,[3-6] but their direct photocopolymerizations have not yet been studied except for the work[1] in this laboratory.

This subject is interesting in connection with the direct photooxygenation reaction, which has been studied in only a few works,[7-9] in contrast to the extensive studies of the photosensitized oxygenation.[10]

Experimental

Materials. The monomers and oxygen were purified as has been described previously.[1]

Polymerization. The apparatus used for the copolymerization of **1** with oxygen[1] was adopted, but a polymerization tube made of quartz was used for all the copolymerizations unless otherwise noted in the text. A trap protected from atmospheric moisture by calcium chloride and immersed in a dry ice–methanol bath was added at the outlet of a refluxing condenser to collect the volatile products. After a given time, the unreacted monomers were distilled off through a vacuum line without heating. The residues were weighed in order to determine the yield of polyperoxide. The distillate was treated with an aqueous semicarbazide hydrochloride solution containing potassium acetate.

Photoirradiation. Photoirradiations were carried out using one of the following three lamps; a Riko 30-watt low-pressure mercury lamp (Model UVL-30A), a Toshiba 100-watt high-pressure mercury lamp (Model SHL-100UV2), and an Ushio 2000-watt xenon lamp (Model UXL-2003D). The wavelength was controlled by means of a Toshiba colored glass filter or a monochrometer (Ritsu Applied Optics Co., Ltd., Model MC-30). In the latter case, the distances from the lamp to the entrance slit of the monochrometer and from the exit slit to the polymerization tube were 21 and 27 cm, respectively. The width of both the slits was 8 mm.

Measurements of Light Intensities. The light intensities of the Xe-lamp at arbitrarily chosen wavelengths were determined by means of a potassium tris(oxalato)ferrate(III) actinometer,[11] using the apparatus for the copolymerization. The results are illustrated in Fig. 1. The light intensities of the low-pressure mercury lamp with and without the application of an UV-29 filter are also given in Fig. 1. The quantum efficiency at 253.7 nm of the actinometer was used for the calculation of the photointensities of the lamp, though it irradiates light of various wavelengths.

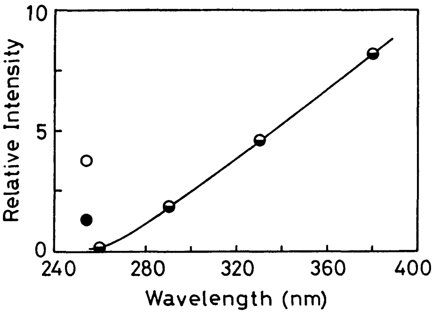

Fig. 1. Photointensities of a xenon lamp (◒) and a low pressure mercury lamp with an UV-29 filter (●) and without it (○). Light detected for the low pressure mercury lamp under the application of the filter consists of higher wavelength bands than the emission band at 253.7 nm because of the almost complete shielding of it by the filter, but the photointensity was depicted at the wavelength for convenience. Distance between light and polymerization tube was 10 cm for the mercury lamp and see experimental section for the xenon lamp.

Measurements of Spectra and Viscosity. Measured as has been described previously.[1)]

Results and Discussion

The amount of residue after the evaporation of the unreacted **1** from the reaction mixture is plotted *versus* the wavelength of the light irradiated in Fig. 2. The absorptions of **1** saturated with nitrogen and oxygen are also illustrated in Fig. 2. The yield of the copolymer increases with an increase in the wavelength of the irradiated light and then decreases after attaining a maximum at about 335 nm, though the intensity of the light increases as the wavelength becomes longer, as is shown in Fig. 1. The photointensity in the shorter-wavelength region is too weak to deduce a conclusion in connection with the intensity of light and the polymer yield. Therefore, the copolymerization was undertaken under the irradiation by the low-pressure mercury lamp. Its most prominent emission band, at 253.7 nm, is in the region where **1** has a strong absorption. The results are shown in Table 1. The emission intensity of the mercury lamp is comparable with that of the Xe-lamp at 320 nm (Fig. 1), but the polymer yield is only one-third of the yield by the Xe-lamp at that wavelength. The application of the UV-29 filter which cuts off emission at 253.7 nm did not reduce the polymer yield, as was expected from the decrease in the photointensity. Further, it must be noticed that the filter also lowers the light intensity at longer wavelengths to some extent. These results suggest that the polymer obtained by using the low-pressure mercury lamp is mainly due to the absorption of light at the longer wavelengths irradiated from the lamp. The alternating copolymer of **1** with oxygen decomposes to produce benzaldehyde and formaldehyde when exposed to ultraviolet light.[12)] The yields of benzaldehyde, determined as its semicarbazone, are also plotted *versus* the wavelength of the light irradiated in Fig. 2. The formaldehyde was qualitatively identified as paraformaldehyde when the white powder detected in the cold trap of the outlet was analyzed by comparing its IR spectrum with that of an authentic sample. It has already been confirmed that these decomposition products do not contribute to the initiation reaction of the copolymerization.[1)]

A similar investigation was carried out for **2**. The dependence of the yield of the residue on the wavelength of the light irradiated is shown in Fig. 3, together with the absorption spectra of **2** saturated with nitrogen and oxygen. The residue was confirmed to be an alternat-

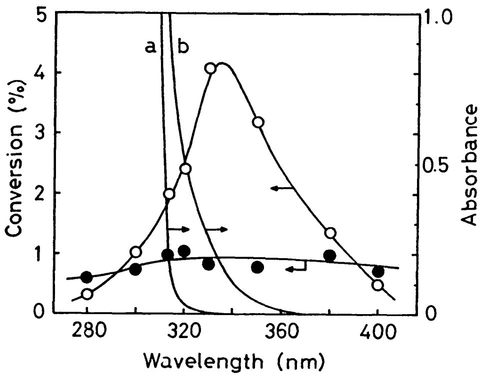

Fig. 2. Electronic spectra of **1** saturated with nitrogen (a) and oxygen (b), and the dependence of the reaction products on the wavelength of the light irradiated. ○: Copolymer, ●: benzaldehyde. Conversions for these compounds were determined based upon **1**. Time 9 h, temp 30 °C, and oxygen 18.5 ml/min.

Table 1. Photocopolymerization of oxygen with **1** and **2** by means of a low-pressure mercury lamp[a)]

Monomer	Filter	Conv. %	BA[b)] %	APH[c)] %
1	—	0.8	0.6	—
1	UV-29	0.5	0.7	—
2	—	1.3	—	0.9
2	UV-29	0.8	—	0.7

a) Temp, 30°C; time, 9 h; oxygen, 18.5 ml/min; distance between light and polymerization tube, 10 cm. Conversion and yield of BA and APH were determined based upon monomers. b) Benzaldehyde. c) Acetophenone.

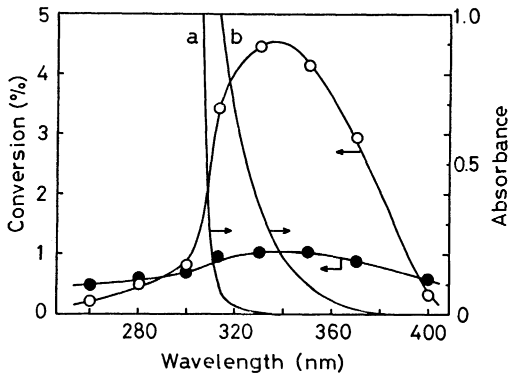

Fig. 3. Electronic spectra of **2** saturated with nitrogen (a) and oxygen (b), and the dependence of the reaction products on the wavelength of the light irradiated. ○: Copolymer, ●: acetophenone. Conversions for these compounds were determined based upon **2**. Conditions are the same as described in Fig. 2.

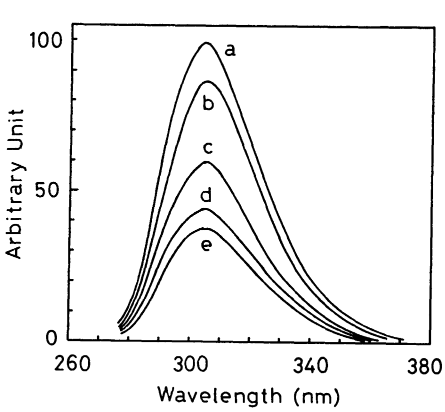

Fig. 4. Fluorescence of **2**. Solvent *n*-hexane, concentration 2×10^{-4} mol/l, excitation 265 nm. Partial pressure of oxygen in the mixture of nitrogen and oxygen: a 0, b 0.2, c 0.5, d 0.8, and e 1.0.

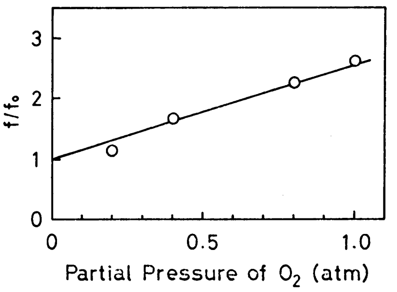

Fig. 5. Stern-Volmer plot of fluorescence at 305 nm for **2**-oxygen system. Conditions are the same as described in Fig. 4.

ing copolymer of **2** with oxygen, based upon its IR spectrum and that of an authentic sample.[5] The results obtained by using the low-pressure mercury lamp as a light source are given in Table 1. These results indicate that the photoabsorption of the CT-band between **2** and oxygen is responsible for the formation of the alternating copolymer, while that of **2** does not contribute to the copolymerization.

Based upon the quenching process of the fluorescence of **1** by oxygen, it has been considered that the exciplex of the excited singlet **1** with oxygen also contributes to the photoinduced alternating copolymerization of **1** with oxygen.[1] However, the results obtained in this work are in contrast to this suggestion. For this reason, the interaction of oxygen with the singlet excited state of **2** has been investigated by measuring the fluorescence spectra of **2** in the presence of oxygen under various pressures. As is shown in Figs. 4 and 5, the fluorescence of **2** is quenched by oxygen according to a Stern-Volmer plot, though it is not quenched so effectively as in the case of **1** under the conditions described. Accordingly, it appeared that the interaction between the singlet excited state and oxygen does not contribute to the initiation reaction of the copolymerization in the case of **2**, either.

The alternating copolymer of **2** with oxygen decomposes to yield acetophenone and formaldehyde on photoirradiation.[5] The former was, in fact, detected in the distillate of the unreacted monomer as its semicarbazone. The white solid precipitated in the cold trap was identified as paraformaldehyde by measuring the IR spectra. The yield of acetophenone was determined quantitatively; it is plotted against the wavelength in Fig. 3. The addition of one-fourth of the maximum yield of acetophenone to the polymerization system did not cause any change in the yield of polyperoxide as compared with the polymerization under normal conditions, *i.e.*, the copolymerization without acetophenone. The polyperoxide thus formed acts as an initiator for the photocopolymerization, as is shown in Table 2, but the results indicate that the initiation of the copolymerization proceeds more effectively through the excitation of the CT-band than the initiation through peroxide.

Thus, the photoabsorption of the CT-bands plays a fundamental role in the copolymerization of oxygen with **1** and **2**, and the excited singlet states of both the monomers do not contribute to the copolymerizations.

TABLE 2. PHOTOCOPOLYMERIZATION OF **2** WITH OXYGEN BY MEANS OF A HIGH-PRESSURE MERCURY LAMP IN A HARD GLASS AMPOULE[a]

Polyperoxide[b] %	Conv. %	APH[c] %
0	8.8	4.0
3.0	13.9[d]	7.4

a) See footnote of Table 1. b) Alternating copolymer of **2** with oxygen. c) Acetophenone. d) Polyperoxide added was not subtracted.

However, the maximum polymer yield is slightly shifted to a longer wavelength region than the wavelength expected from the CT-bands. One reason for this is the fact that the intensity of the irradiated light decreases with the decrease in the wavelength. The other is the absorption of light by **1** and **2**, which does not contribute to the reactions, because the sharp decrease in the polymer yield begins at the wavelength where the absorption bands of **1** and **2** appear.

The contribution to the copolymerizations by the triplet states excited directly by the singlet states of **1** and **2** is excluded on the basis of the following considerations. The singlet-triplet transition of **1** has been observed around 463 nm,[13] while that of **2** is expected to be detected at a longer wavelength region judging from the effect of the substituents on the transition of aromatic and olefinic compounds,[14] though the datum for the singlet-triplet transition for **2** is not available.

The reduced viscosities measured for the copolymers of oxygen with **1** and **2** were found to be in the region from 0.06 to 0.08 dl/g. The values were scattered, without any significant trend with respect to the polymerization conditions.

Financial support (Grant-in-Aid No. 975439) by the Ministry of Education, Japanese Government, is acknowledged.

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