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# Dependence of Photodegradation of Poly(2,6-dimethyl-1,4-phenylene oxide) on β-Relaxation Role of Solubility of Oxygen in Photooxydation

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## ABSTRACT

The dependence of the rate constants of photoinitiated oxidation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and of oxygen consumption during this reaction have been ivestigated. The obtained results point out that the changes in the values of the rate constants for both reactions are related to the β-relaxation processes observed in PPO at the same temperature range. The consideration of this effect and of its influence on oxygen solubility in PPO leads to explanation of the determined values of apparent activation energies for PPO photooxidation.

## INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) shows a very high α-relaxation temperature $T_g = 225^oC$. The γ-relaxation, about $-240^oC$, which is related to rotation of methyl groups and the β-relaxations due to oscilation of aromatic ring around C-O-C bonds were observed EISENBERG, CAYROL (1971), DE PETRIS et al. (1967), ALLEN et al. (1970) in a wide range of temperatures. The weak β-relaxation appears in dynamic mechanical properties study in a temperature range of $-17^oC$ and $97^oC$ DE PETRIS et al. (1967). In viscoelastic properties investigations it appears at temperature range $-40^oC$ and $20^oC$ EISENBERG, CAYROL (1971) and at $80^oC$ when studied by NMR ALLEN et al. (1970). In all these investigations a drastic effect of sample thermal history on β-relaxation was observed.

We have shown in our previous paper WANDELT, KRYSZEWSKI (1980) that the rate of chain scission reaction occuring in photodegradation of thin films of polystyrene depends on pre-Tg relaxations (related to mobility of small units in polymer chain). This effect was attributed to limited concentration of oxygen, controlled by the mobility of polymer chains.

This paper reports some results of our studies on the role of oxygen solubility and mobility of chain elements in photooxidation of PPO. PPO is a suitable

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material for these studies since it shows the -relaxations,connected with oscillation of aromatic group, in convenient temperature range. The mobility of chain elements seems to be important in photooxidation and in transport of oxygen inside of polymer film. It seems to be generally agreed that the photooxidation of poly(2,6-dimethyl-1,4-phenylene oxide) is related to photooxidation process of methyl groups followed by hydroperoxide formation and their subsequent decomposition. The resulting macromolecules and crosslinked polymer contain carbonyl groups as a main product of hydrperoxide decomposition WANDELT et al. (in press).

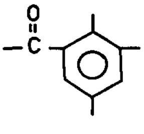
## EXPERIMENTAL

Poly(2,6-dimethyl-1,4-phenylene oxide) of $M_w$=44000 and $M_n$ = 25000 was purified by dissolution in chloroform followed by precipitation in pure methanol (three times) and drying in vacuum for 48 hours. The polymer films cast from chloroform were irradiated by high pressure mercury lamp with maximum emission at 254 nm. which corresponds to the region of high absorption of PPO WANDELT et al. (in press). The light intensity incident on the polymer film surface was $I_o$ = 5,2 x $10^{-9}$ E $cm^{-2}s^{-1}$. Oxygen absorption measurements during irradiation were conducted with slightly modified Grassie s GRASSIE, WEIR (1965) method.

## RESULTS AND DISCUSSION

It was shown in our previous paper WANDELT et al. (in press) that the rate constant of oxygen uptake during photoinitiated oxidation of PPO depends linearly on pressure of oxygen after a short period. It means that the oxidation is controlled by concentration of oxygen dissolved inside polymer film. The results of oxygen consumption measurements during photooxidation of PPO (600 mm Hg of oxygen pressure) as a function of temperature of irradiated sample, are shown in Fig.1. The dependence of rate constant of oxygen uptake $k_{O_2}$ on temperature increases nonlinearly in the range of temperature higher than 50°C, which we attribute to -relaxation.

It was established by us in our previous paper WANDELT et al. (in press) that the increase of absorption broad band in the UV spectrum with maximum at 303 nm is related to absorption of carbonyl groups, which are the main product of photooxidation of PPO. It concerns the soluble fraction (linear polymer chains) as well as the crosslinked polymer



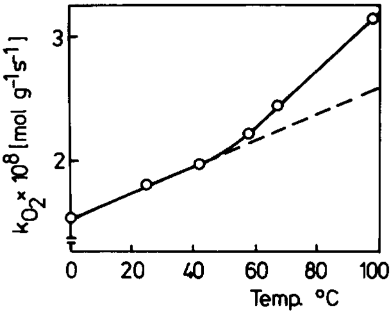


Fig.1.-Dependence of rate constant of oxygen consumption on temperature of irradiated sample of PPO. The oxygen pressure p=600 mm Hg.

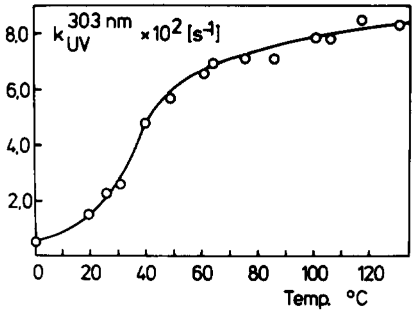


Fig.2. Dependence of rate constant of oxidation $k_{UV}$( 303 nm) on temperature.

The studies WANDELT et al. (in press) of mechanism of photooxidation of PPO allow us to assume that the rate constant of carbonyl concentration change is proportional to the rate constant of oxidation reaction of PPO. The dependence of the rate constant of oxidation on temperature, presented in Fig.2, shows similarly an abnormal increase at the temperature range 30-60°C. Arrhenius plots were derived for these two rates of oxidation reaction and are shown in Fig.3. The plots change their slopes at about 50-45°C, with various energy of activation (see Fig.3).

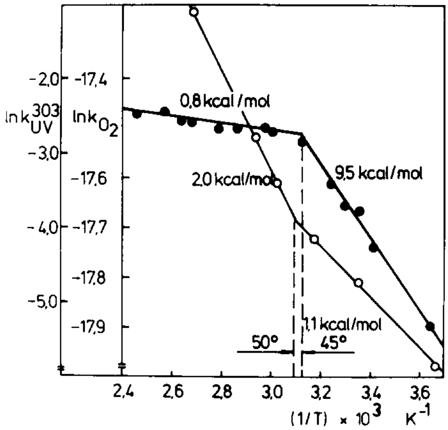


Fig.3. Arrhenius plots for two rate constants of photooxidation of PPO: oxygen absorption $k_{O_2}$ and oxidation reaction $k_{UV}$ (303 nm).

Solution of equation of oxygen consumption during oxidation reaction with simultaneous diffusion of oxygen was given by several authors CRANK (1975), BILLINGHAM, WALKER (1975). For the thin films of polymer (we used 20 μm) the rate of oxygen consumption,referred to 1g of polymer, may be written

$$k_{O_2} = k\ C_o/d \qquad (1)$$

where: k is the rate constant of oxidation = $k_{UV}$ (303nm) WANDELT et al.(in press), $C_o$ is the concentration of oxygen at the polymer film surface, d is the density of polymer.

Relation between concentration of dissolved gas $C_o$ and the solubility S, in agreement to Henry's low, permitted us to calculate the solubility with the use of the following equation:

$$k_{O_2} = \frac{k\ S\ p\ 273}{d\ 22400\ 76\ T} \qquad (2)$$

where: p is the pressure of the gas phase above the film surface.

Fig.4 shows the solubility of oxygen as a function of temperature. The determined values of oxygen solubility in PPO film can be accepted in comparison with data of Amerongen VAN AMERONGEN (1950).

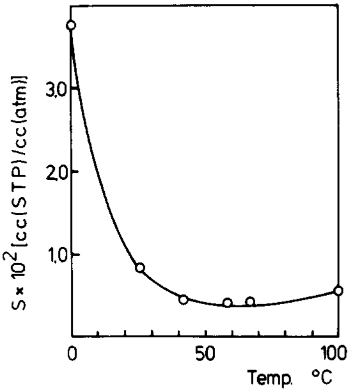


Fig.4. Dependence of solubility of oxygen in PPO films on temperature.

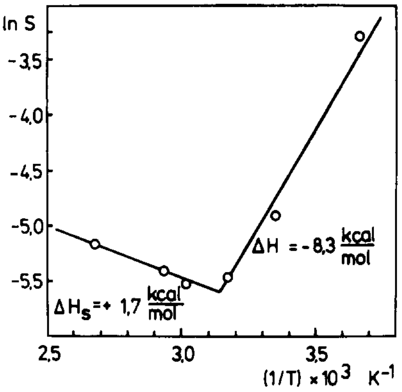


Fig.5. Arrhenius plot of solubility of oxygen in PPO.

The Arrhenius plot for solubility of oxygen is shown in Fig.5. The heat of oxygen dissolution, calculated from this plot, appears to be negative at lower temperature region and changes to positive values at about 50°C. In agreement to eq.2 the energy of activation of oxygen consumption we can write as a sum of energy of activation of oxidation and heat of solution of oxygen

$$E_{O_2} = E\ \text{oxidation} + \Delta H_s \qquad (3)$$

The experimental values of activation energy for $k_{O_2}$ and calculated with the use of eq.3 are in good agreement as follows from the data given in Table 1

TABLE 1. Experimental and calculated activation energy values for rate constants of oxygen consumption ($k_{O_2}$)

| Range of temperature | $E_{O_2}$ (exp.) | $E_{O_2}$ (calc.) |
|---|---|---|
| 0 - 50°C | $1,1\times10^3$cal/mol | $1,2\times10^3$cal/mol |
| 50 - 98°C | $2,0\times10^3$cal/mol | $2,5\times10^3$cal/mol |

## CONCLUSIONS

The presented results of the studies on photooxidation of poly(2,6-dimethyl-1,4-phenylene oxide) allow us to formulate some conclusions on the physical aspects of photooxidation of this polymer.

The course of photoinitiated oxidation reaction of PPO depends on mobility of one mere unit in polymer chain. The fast increase of the rate constant of photooxidation reaction of PPO i.e. the increase of the rate constant of carbonyl group formation and of crosslinking reaction, which will be discussed in the next paper, occurs at the temperature range of 45-60°C which corresponds to the $\beta$-relaxation phenomena.

The mobility of a mere unit in polymer chain influences the transport and the distribution of oxygen inside the polymer even so the solubility of oxygen decreases with the rising temperature. Decrease of oxygen solubility and the negative value of the heat of solubility cause the apparent decrease of activation energy of PPO photooxidation process below $\beta$-relaxation temperature. The small increase of solubility of oxygen and simultaneous increase of heat of solution in the temperature range 50 - 90°C increase apparent activation energy values above the $\beta$-relaxation. These results show that the consideration of the pre-Tg relaxations are important in analysis of photooxidative degradation of amorphous polymers.

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