

POLYMER OXIDATION IN GLASSY STATE

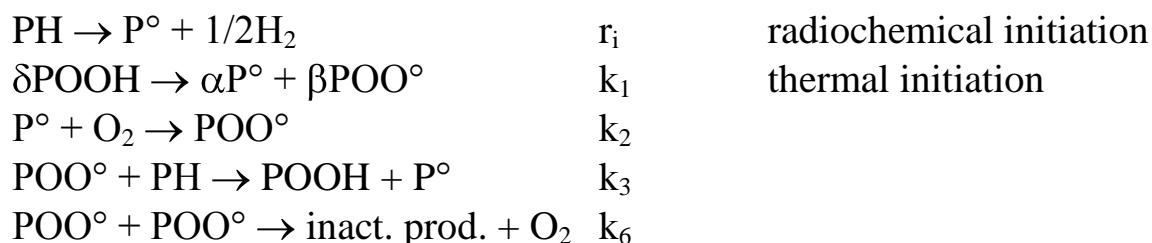
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Most of the fundamental literature on polymer oxidation deals with polyolefins and elastomers, i.e. with polymers in which the reacting rubbery phase is stirred by ample cooperative motions favoring the diffusion of radicals and the homogenization of the reactive medium. This paper deals with the oxidation glassy polymers through a discussion of orders of magnitude of initiation or termination rate constants. Data obtained for several polymers oxidized below T_g will be reviewed assuming that their oxidation is described by the following model:



Radiooxidation of PEEK and PSU at ca $60^\circ\text{C}^{1,2}$ was monitored oxidation profile in thickness by FTIR. From a classical diffusion reaction theory, the thickness of oxidized layer can be linked to the ratio k_3^2/k_6 . This was found surprisingly high for those aromatic thermostable polymers. k_3 is linked to the C-H bond dissociation energy and is thus very low so that k_6 is very low also (on the order of unity) instead of 10^5 - $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for PP or PE.

Polycyclopentadiene ($T_g \sim 160^\circ\text{C}$) is a very oxidizable polymer in which maximal POOH concentration recorded by DSC coupled with specific SO_2 treatment is reached in less than 1 hour for thermal ageing at 90°C (Figure 1) and induction period for carbonyl clearly 10 or 100 times shorter than for BR³, IR⁴, PP⁵ or PE⁶. Hydroperoxides analysis by DSC suggested $\Delta H = 200 - 1000 \text{ kJ mol}^{-1}$ as decomposition enthalpy per mole of POOH⁷ so that

$[\text{POOH}]_{\text{max}} \sim 1 \text{ mol l}^{-1}$ which is for example 5 times higher than for PP in the same conditions.

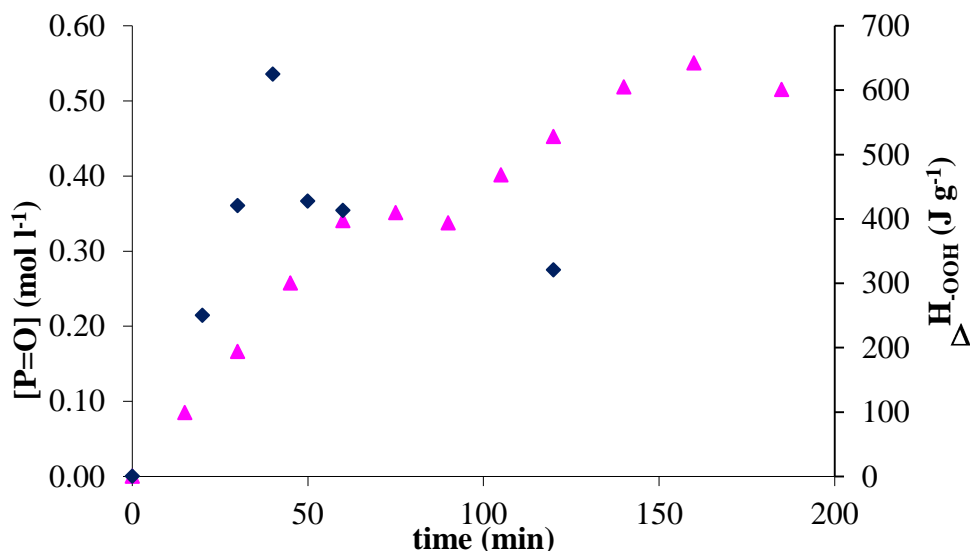


Figure 1 Carbonyl concentration and enthalpy of hydroperoxides thermal decomposition for PCPD ageing at 90°C.

The low induction period is explained by high k_1 value⁸ meanwhile it is easy to show that $[\text{POOH}]_{\text{max}}$ depends on the ratio $k_3^2/(k_6.k_1)$ which suggests that k_6 is low here also.

These observations militate in favor of a control of termination kinetic by the low mobility of radicals at glassy state which is slower than expected for the bimolecular process between two radicals.

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