High pressure effect on polyethylene crosslinking initiated by benzoyl peroxide

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High pressure effects (300, 600, and 800 MPa) on polyethylene crosslinking initiated by benzoyl peroxide have been studied at 120°C. An increase in pressure leads to a decrease in yield of the insoluble gel; the yields at 300, 600, and 800 MPa were respectively 96, 86, and 79%. With increasing pressure the rate of polyethylene crosslinking decreases and the rate of benzoyl peroxide decomposition at 300, 600, 800 MPa can be anticipated from the time of crosslinking. The activation volume $\Delta V^{\ddagger} = 9.1$ cm^3 mol^{-1} was determined for benzoyl peroxide decomposition on polyethylene at 120°C.

INTRODUCTION

The rate of the decomposition of radical initiators[1-5] and of termination reactions is known to decrease with increasing pressure both in liquid solvents and in polymers[5-8]. Although pressure increases the rate of transfer reaction[9], the first two partial reactions of polymer crosslinking are decisive. In radiation initiated crosslinking we observed for an ethylene–propylene copolymer a rise in the gel yield with increasing pressure. The pressure effect is not assigned to an increase in the efficiency of the formation of crosslinks between polymer chains but to a lowering of the probability of chain scission resulting from suppression of molecular motion[10]. According to Milinčuk *et al.*[11] pressure even lowers the radiation yield of radicals in a series of polymers. A decrease in the radiation polyethylene crosslinking has also been observed.

The aim of this paper has been investigation of the effects of high pressure (pressures between 300 and 800 MPa) on the rate of crosslinking and on the yield of the crosslinking polyethylene using benzoyl peroxide as initiator.

EXPERIMENTAL

Polyethylene, type Bralen RB 03-23, $M_w = 130\,000$, produced by Slovnaft Bratislava, was used. It was dissolved in xylene before use at boiling temperature of xylene and then precipitated with methanol giving powder polyethylene.

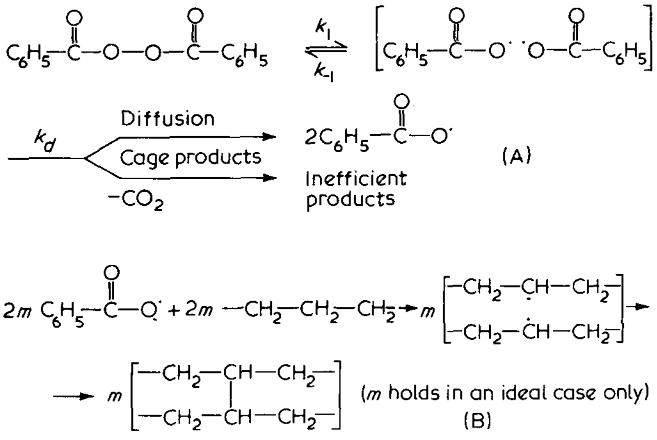
Benzoyl peroxide, product of Argon Lodž (Poland), was purified by triple purification from chloroform solution with anhydrous methanol and removal of solvent residues in a vacuum drier at room temperature.

Powder polyethylene was allowed to impregnate in a chloroform solution of benzoyl peroxide for 24 h in the dark and then the solvent was removed by blowing with warm air (to 40°C) and evaporating at reduced pressure. The ratio between polyethylene and benzoyl peroxide solution has been chosen so as to achieve the required content of benzoyl peroxide in the polymer after solvent evaporation.

The crosslinking of polyethylene was performed as follows: the sample of polyethylene containing benzoyl peroxide was put into a steel pressure device, pressed to the required pressure and held at this pressure at constant temperature. The pressure and temperature were automatically regulated. Rapid heating and cooling of the pressure device was secured by a temperature impulse with sharp edges. After cooling and pressure release, the cylindrical sample was taken from the pressure device described previously[12] and allowed to extract in boiling xylene containing antioxidant for 36 h. After extraction, the insoluble part of the sample was washed with benzene and dried. This part of the sample was the crosslinked polyethylene gel.

RESULTS AND DISCUSSION

The scheme shows the polyethylene crosslinking initiated by radicals:



(*m* holds in an ideal case only)

The time dependence of the polyethylene crosslinking initiated by radicals formed in the thermal decomposition

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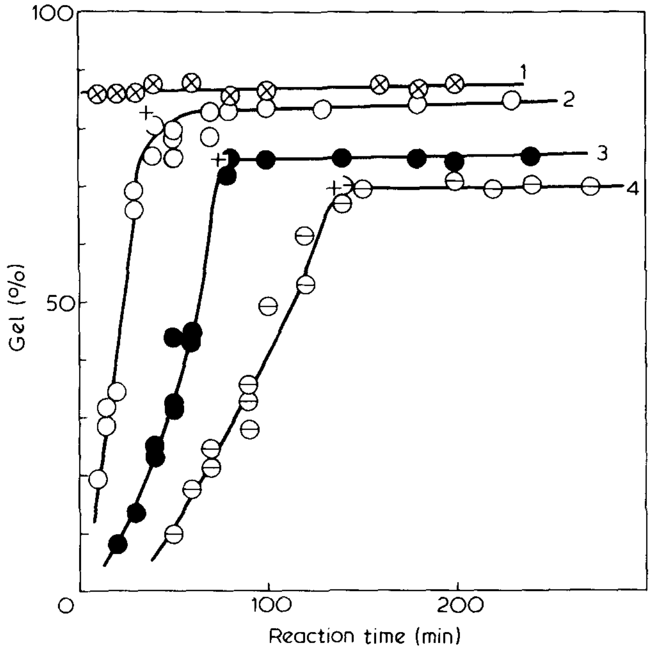

Figure 1 Plot of the gel content (wt %) in polyethylene against reaction time of crosslinking (min) at 120°C, 3% (wt) initial benzoyl peroxide content and various pressures: (1), 0.5 MPa; (2), 300 MPa; (3), 600 MPa; (4), 800 MPa

of benzoyl peroxide was observed at 120°C. The higher the pressure applied in the crosslinking, the slower is the increase in the insoluble gel in crosslinking polyethylene (curves 2, 3, 4 in *Figure 1*). The decreasing rate of the polyethylene crosslinking with increasing pressure can be accounted for by the lowering rate of the production of primary peroxide radicals resulting from the increasing polymer viscosity and also the cage effect (a rise in the rate constant for recombination, k_{-1}, scheme A). The practically horizontal parts of the curves 2, 3, and 4 show that the gel content does not vary with the reaction time, i.e. only negligible residues of peroxide might remain in the polymer. For further considerations and calculations we determined proper crosslinking times, i.e. the reaction time during which the benzoyl peroxide concentration falls below the critical value. The proper crosslinking periods consist of the time from the beginning of the reaction to intersections of individual plots marked with a cross in *Figure 1*. The points of intersection were obtained by prolonging both linear segments of plots, i.e. the segment after which the gel content increases and the segment where the gel content is stabilized.

Preceding considerations on the possible existence of peroxide residue after the crosslinking time in calculation of the rate constant for benzoyl peroxide decomposition of the first order of magnitude, k_d, in polymer led to an assumption that of the total amount of peroxide, i.e. 0.12385 mol kg^{-1} (3 wt%), only 0.11765 mol kg^{-1} (2.85%) is decomposed.

Table 1 contains the values of k_d calculated for benzoyl peroxide decomposition in polyethylene at 300,600, and 800 MPa and 120°C. Graphical solution of the relation (C) (13):

$$\frac{\mathrm{d}\ln k_d}{\mathrm{d}P} = -\frac{\Delta V^{\neq}}{RT} \qquad \text{(C)}$$

using the data from *Table 1* gave a positive value of the activation volume $\Delta V^{\neq} = 9.1$ cm^3 mol^{-1} of the benzoyl peroxide decomposition in polyethylene (*Figure 2*). As has already been found, pressure increases the viscosity of most liquids, diffusion constants decrease with increasing viscosity and therefore pressure retards reactions of homolytic scission; this is seen on the positive value of the activation volume $\Delta V^{\neq}$ of these reactions[1,14]. Reactions in which identical radicals are formed by a simple bond fission should generally be characterized by an increase of the volume in the transition state; here $\Delta V^{\neq}$ is about 10 cm^3 mol^{-1} (ref. 14). The value of $\Delta V^{\neq} = 9.1$ cm^3 mol^{-1} is found in the expected region. The observed $\Delta V^{\neq}$ does not correspond in our case of decompoisition only to the activation volume of homolytic fission (k_1) but it also includes recombination (k_1) in scheme A and the activation volume needed for radical decay from cage or their decomposition in the cage into non-radical products[1,14]. From the plot in *Figure 2* we obtained the extrapolated value of the rate constant for benzoyl peroxide decomposition at normal pressure (0.1 MPa) and temperature of 120°C; $k_d = 3.2 \times 10^{-3}$ s^{-1}. The extrapolated value of the constant is according to Rado and Lazár[15] 2.6×10^{-2} s^{-1}. A much higher value of the extrapolated constant[15] is probably caused by the linear extrapolation (ln k_d as a function of $1/T$) that was done from temperature of 98.4 and lower to 120°C; i.e. from temperatures at which the polymer is in the solid phase to

Table 1 Rate constants for benzoyl peroxide decomposition $-k_d$ in polyethylene and contents of undissolved gel in polyethylene at high pressures and 120°C (3% initial benzoyl peroxide content)

Pressure	Proper time of the cross-linking (min)	Gel content[a] (weight %)	k_d (s^{-1}/x 10^4)	ln k_d
0.1	–	87[b]	31.82[c]	−5.75
300	36	84	13.63	−6.598
600	74	75	6.63	−7.318
800	136	69	3.61	−7.926
300[d]	37	95	13.26	–

[a] After 200 min of reaction time of crosslinking
[b] At 0.5 MPa
[c] Extrapolated value from *Figure 3*
[d] At 6% initial benzoyl peroxide content

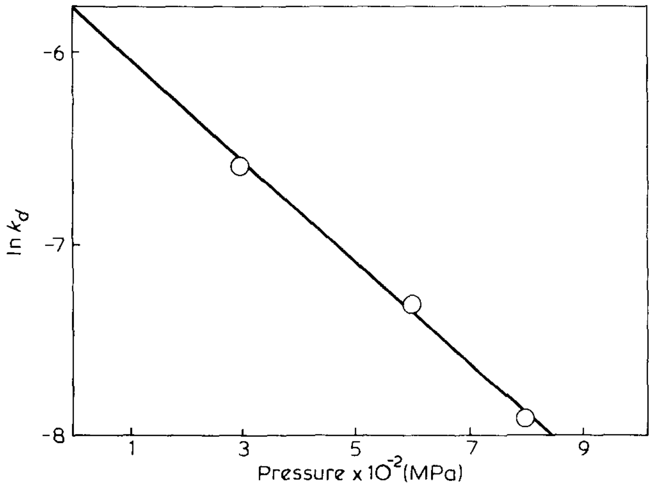

Figure 2 Plot of natural logarithm of the rate constant for benzoyl peroxide decomposition k_d against pressure (graphical solution of relation A)

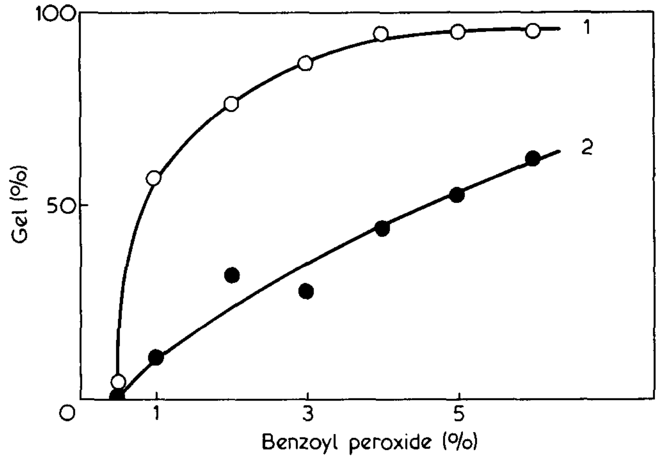

Figure 3 Plot of the gel content (wt %) in polyethylene against initial benzoyl peroxide content (wt %) at 120°C; time of crosslinking 100 min: (1) at 0.5 MPa; (2) at 800 MPa

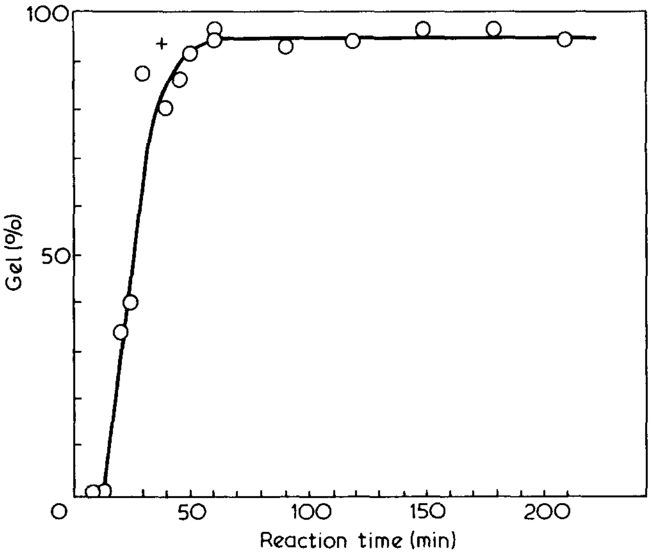

Figure 4 Plot of the gel content (wt %) in polyethylene against reaction time of crosslinking (min) with 6% initial benzoyl peroxide content at 120°C and 300 MPa

temperatures where the polymer is in melt. The extrapolated value of 4.6×10^{-3} s^{-1} was found[16] for the rate constant of benzoyl peroxide decomposition k_d in benzene.

Plots in *Figure 1* provide information about the high pressure effect on the yield of crosslinking polyethylene (gel) at the same initial benzoyl peroxide concentration. If we consider the highest yield of gel, i.e. without subjecting to high pressure, as unity (curve 1, *Figure 1*), then at 300 MPa the yield is only 0.96, at 600 MPa 0.86, at 800 MPa 0.79 (read at 200 min of crosslinking from *Figure 1*). This can be explained by the fact that the increase in polymer viscosity subjected to pressure increases the amount of non radical reaction products in the cage which are no longer able to dissociate into radicals (scheme A). The yield of gel can be also lowered by the fact that with increasing polymer network and by subjecting to pressure, the segment motion of macromolecules decreases together with recombination between polymer radicals under formation of crosslinks[17].

Figures 3 and *4* show that a rise in the peroxide content in polymer leads to a higher final gel content even when subjected to high pressure. That is, the pressure effect on the increase in the amount of non-radical products (cage effect) is compensated by higher peroxide content. For 6% initial peroxide content in polyethylene, the gel content (95%) obtained at 300 MPa (*Figure 4*) was higher than that at 300 MPa and 0.5 MPa for 3% initial benzoyl peroxide content (*Figure 1*, curve 1).

The time of crosslinking found when applying 6% benzoyl peroxide content and pressure 300 MPa, is 37 min (*Figure 4*, *Table 1*). This is close to the time obtained at the same pressure and 3% benzoyl peroxide content, i.e. 36 min. We can thus assume that the induced benzoyl peroxide decomposition in polymer is suppressed when subjected to pressure. A similar conclusion was drawn by Neuman, Jr. and Behar[18] from an analysis of decomposition products of t-butylphenylperacetate and carbo-t-butylcyclohexane in cumen and chlorobenzene at 400 MPa.

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