# Efficiency of polyfunctional monomers in polypropylene crosslinking by various peroxides

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*Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday*

The efficiency of crosslinking of isotactic polypropylene by radicals formed by thermal decomposition of organic peroxides was studied in the presence of polyfunctional monomers. Four peroxides and nine kinds of polyfunctional monomers were used. The results showed that the yield of the gel in crosslinked isotactic polypropylene is proportional to the number of functional groups in polyfunctional monomer and to the reactivity of peroxide used.

When using benzoyl peroxide in the presence of pentaerythritol tetraallyl ether and furfuraldehyde pentaerythrityl acetal, the gel yield was strongly suppressed as a result of deactivation of the polyfunctional monomer by primary radicals.

Изучена эффективность сшивания изотактического полипропилена радикалами, образующимися при термическом разложении органических перекисей, в присутствии полифункциональных мономеров. Использовались четыре различные перекиси и девять видов полифункциональных мономеров. Результаты показали, что выход геля в случае сшитого изотактического полипропилена пропорционален числу функциональных групп в полифункциональном мономере и реакционной способности используемой перекиси.

При использовании перекиси бензоила в присутствии тетрааллилового эфира пентаэритрита и пентаэритритилацеталя фурфуральдегида образование геля было сильно подавлено вследствие дезактивации полифункционального мономера первичными радикалами.

The efficiency of polypropylene crosslinking by radicals formed by thermal decomposition of peroxides is relatively low. One of the possibilities of increasing the efficiency of peroxide crosslinking of polypropylene is the use of coagents, such as sulfur [1—4], quinone [5], and polyfunctional monomers. By applying these reactants, the crosslinking efficiency was found to depend on the mole ratio between peroxide and coagent. In our previous paper [6] we used as coagent — in thermal crosslinking of polypropylene by dicumyl peroxide —

polyfunctional monomers containing double bonds carbon—carbon. Polyfunctional monomers with higher number of functional groups were found to be most effective. This was explained by the possibility of joining macroradicals from the decomposing polypropylene to the reactive molecules of polyfunctional monomers which form bridges between polymeric chains.

In the case of polypropylene crosslinking without addition of coagents the crosslinking efficiency depends on the kind of peroxide used [7].

In this paper we studied the effect of polyfunctional monomers on the action of various peroxides during crosslinking which has not yet been investigated in detail.

## Experimental

### *Materials*

Unstabilized powdered polypropylene (fibre-forming Tatren HPF type, product of Slovnaft, Bratislava) was used for crosslinking. The powdered polymer was sieved for 6 h through a series of sieves. The crosslinking in the presence of various monomers was performed with a polypropylene fraction passing through square openings of 0.71 mm sides and held on a sieve with square openings (0.5 mm).

The commercial products (divinylbenzene, ethylene glycol dimethacrylate, methacrylallyl ester, Fluka A.G.; diallyl phthalate, BDH Chemicals, Ltd.; triallyl cyanurate, Schuchhardt) and the compounds prepared in the laboratory (furfuraldehyde pentaerythrityl acetal, acrylaldehyde pentaerythrityl acetal, and pentaerythritol tetraallyl ether) were used as polyfunctional monomers.

Dicumyl peroxide, Akzo Chemie, *tert*-butyl perbenzoate, Merck, 2,5-dimethyl-2,5--di(*tert*-butylperoxy)hexane, Luperox, GmbH, and dibenzoyl peroxide, Fluka, were used as initiators.

### *Sample preparation*

Powdered polypropylene was impregnated with a chloroform solution of polyfunctional monomer and peroxide at laboratory temperature for 24 h in a closed dark bottle. The solvent was then removed from a mash-like mixture of reactants by air flow under constant stirring of the polymers. After obtaining the powdered consistency of the polymer, the sample was dried to constant mass in a vacuum drier at 40 °C.

### *Crosslinking*

Polypropylene containing reaction components was sealed in glass test tubes filled with nitrogen. The tubes were annealed for 1 h in an oil bath at 170 °C.

## Extraction of uncrosslinked polymer

The gel content was determined by 14 h extraction of crosslinked polypropylene in boiling xylene. Before introducing into the solvent, the polymer samples were packed in the glass-fibre fabric, labelled, and weighed. During extraction, the solvent was changed every two hours. A small amount of hydroquinone was added simultaneously with pure xylene for thermooxidative stabilization. After completion of the extraction in xylene the samples were extracted for another 4 h in benzene. The packs with samples were then dried at laboratory temperature in a vacuum drier to constant mass.

Three samples were used for determining the insoluble fraction. The $w$ values of the gel content differed from the calculated average by about $\pm (0.5—3.0)\%$.

## Results and discussion

The investigation of the crosslinking of isotactic polypropylene under thermal decomposition of peroxide in the presence of polyfunctional monomer (Table 1) shows that the yield of gel as a function of the type of peroxide increases in most cases in the order from 2,5-dimethyl-2,5-di(*tert*-butyl-

*Table 1*

Gel content in crosslinked polypropylene in the presence of 4 mass % of polyfunctional monomer and 4 mass % of peroxide after 1 h annealing at 170 °C

| Polyfunctional monomer | $f^a$ | $m^b$ | $w$(gel)/% | | | |
|---|---|---|---|---|---|---|
| | | mmol kg$^{-1}$ | L-101 | DCP | BP | TBPB |
| Allyl methacrylate | 2 | 355 | 0.6 | 0.6 | 12 | 26 |
| Ethylene glycol dimethacrylate | 2 | 224 | 5.0 | 12 | 35 | 25 |
| Diallyl phthalate | 2 | 180 | 6.5 | 16 | 20 | 39 |
| Divinylbenzene | 2 | 341 | 14 | 24 | 31 | 37 |
| Acrylaldehyde pentaerythrityl acetal | 2 | 208 | 26 | 30 | 14 | 59 |
| Diallyl maleate | 3 | 226 | 14 | 22 | 37 | 40 |
| Triallyl cyanurate | 3 | 177 | 16 | 24 | 29 | 50 |
| Furfuraldehyde pentaerythrityl acetal | 4 | 152 | 51 | 58 | 2 | 63 |
| Pentaerythritol tetraallyl ether | 4 | 150 | 53 | 59 | 4 | 73 |

*a)* Number of functional groups in a coagent molecule; *b)* molality of polyfunctional monomers. L-101 — 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane, DCP — dicumyl peroxide, BP — dibenzoyl peroxide, TBPB — *tert*-butyl perbenzoate.

peroxy)hexane (L-101), dicumyl peroxide (DCP), dibenzoyl peroxide (BP) to *tert*-butyl perbenzoate (TBPB), where it has the highest value. The presence of polyfunctional monomers as crosslinking coagents has become evident as previously [6] — the gel yield in crosslinked polypropylene increased with the increasing number of functional groups in a molecule of coagents. A different situation arises for the gel yield obtained *via* polypropylene crosslinking by dibenzoyl peroxide in the presence of furfuraldehyde pentaerythrityl acetal (DFAPEA) and pentaerythritol tetraallyl ether (PETA). Dibenzoyl peroxide appears to be at low concentration one of the most efficient peroxides during polypropylene crosslinking [7]. The low efficiency of PETA combined with dibenzoyl peroxide also follows from the measurements of the dependence of the gel content on peroxide concentration (Fig. 1). The crosslinking efficiency in the presence of PETA is even lower than when dibenzoyl peroxide is used alone.

One of the reasons for the low gel yield during polypropylene crosslinking by dibenzoyl peroxide in the presence of PETA might be inhomogeneous dissolution of reactants in the system. In order to secure good solubility of dibenzoyl peroxide and PETA, dioctyl phthalate or trichlorobenzene was added into the reaction mixture. In spite of this arrangement of experimental conditions, gel yields (Table 2) have not significantly increased and agree with the values reported in Table 1. The cause of the low gel yield cannot therefore be assigned to heterogeneity of the reaction system. The polypropylene swelling in PETA confirmed that under the reaction conditions we used for polypropylene crosslinking the added amount of PETA dissolves in the polypropylene sample (already at 150 °C after 1 h in a pressed polypropylene foil more than 12 mass % PETA is dissolved). The improvement of the solubility of reactants in the presence of liquid solvents occurs, excepting *tert*-butyl perbenzoate, for all peroxides; however, the most markedly in the case of 2,5-dimethyl-2,5-di(*tert*--butylperoxy)hexane. A slight decrease in the gel yield of *tert*-butyl perbenzoate
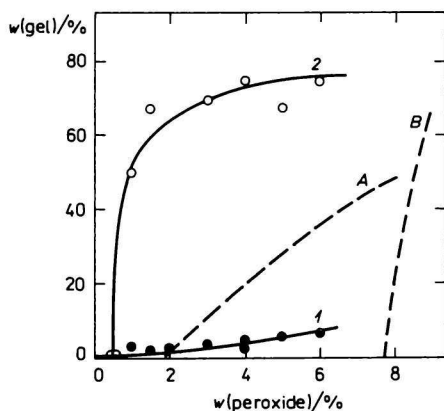


Fig. 1. A plot of the gel content in crosslinked isotactic polypropylene *vs.* BP (*1*) and DCP (*2*) mass fraction at constant $w(\text{PETA}) = 4\%$. *A* — dependence of the gel content on dibenzoyl peroxide mass fraction; *B* — dependence of the gel content on dibenzoyl peroxide mass fraction in the absence of PETA [7]. Reaction temperature 170 °C, time of annealing 1 h.

Table 2

Gel content in polypropylene crosslinked by 4 mass % peroxide and 4 mass % polyfunctional monomer in trichlorobenzene (mass fractions of trichlorobenzene in reaction mixture: a) 4 %, b) 8 %, c) 15 %; d) dioctyl phthalate ($w = 4$ %) used as solvent
Annealing — 1 h, temperature 170 °C

| Peroxide | $w(gel)/\%$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | DVB | PETA | DVB | PETA | DVB | PETA | PETA |
| | a | | b | | c | | d |
| L-101 | 22 | 69 | 25 | 63 | 29 | 66 | — |
| DCP | 29 | 77 | 30 | 82 | 32 | 79 | — |
| BP | 38 | 5 | 35 | 5 | 48 | 5 | 3 |
| TBPB | 35 | 61 | 32 | 57 | 38 | 64 | |

DVB — divinylbenzene, PETA — pentaerythritol tetraallyl ether, L-101 — 2,5-dimethyl-2,5--di(tert-butylperoxy)hexane, DCP — dicumyl peroxide, BP — dibenzoyl peroxide, TBPB — tert--butyl perbenzoate.

Table 3

Values of the gel content in polypropylene crosslinked by thermal decomposition of 4 mass % peroxides (L-101, DCP, BP, TBPB) in the presence of 4 mass % PETA and 2, 4, 6, and 8 mass % dibenzoyl peroxide
Annealing temperature 170 °C, time 1 h

| Peroxide | $w(gel)/\%$ | | | | |
|---|---|---|---|---|---|
| | $w(BP)/\%$ | | | | |
| | 0 | 2 | 4 | 6 | 8 |
| L-101 | 53 | 55 | 45 | 37 | 37 |
| DCP | 59 | 62 | 54 | 46 | 42 |
| BP | 4 | 6 | 10 | 12 | 22 |
| TBPB | 73 | 68 | 62 | 51 | 48 |

probably follows from the dilution effect, which cannot be overlapped by better homogeneity of the system since TBPB alone is well soluble in polypropylene.

Since the low efficiency of the polypropylene crosslinking in the presence of dibenzoyl peroxide is not connected with the heterogeneity of the system, the reason has to be looked for in the reactivity of primary radicals. In the first place, it will be the more efficient reaction of the radical of the decomposing dibenzoyl peroxide with PETA as compared with polypropylene. Thus in view of the formation of crosslinked bonds, consumption of both peroxide and added coagent is inefficient. Formation of macroradicals of polypropylene as precur-

sors of crosslinked bonds is then limited by side reaction of primary radicals with PETA. Deactivation effect of dibenzoyl peroxide is also seen in polypropylene crosslinking in a mixture with other peroxides in the presence of PETA (Table 3). Although on addition of dibenzoyl peroxide, the overall concentration of peroxides in the sample is raised, the gel yield is lowered. The result from this measurement again supports the explanation according to which the reason for the low gel yield is preferential reaction of PETA with low-molecular radicals of the decomposed dibenzoyl peroxide.

Our studies show that during polypropylene crosslinking in the presence of coagents polyfunctional monomer—peroxide, the crosslinking efficiency depends on the use of peroxide and the type of polyfunctional monomer. The optimum concentration of coagents in view of the maximum yield of crosslinked bonds will be determined by the ratio between the reactivity of polypropylene and of polyfunctional monomer and the primary peroxide radical.

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Translated by A. Rebrová