Peroxide-Initiated Crosslinking of Polypropylene in the Presence of *p*-Benzoquinone

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Synopsis

Crosslinking of polypropylene was investigated when initiated by thermal decomposition of organic peroxides. *p*-Benzoquinone was found to be an effective coagent of crosslinking. The efficiency of benzoquinone is about 5 times higher than that of polyfunctional monomers. Almost complete crosslinking of polypropylene can be reached at proper conditions.

INTRODUCTION

Crosslinking of polypropylene initiated by thermal decay of peroxides is more complicated task than similar modification of polyethylene or unsaturated rubber. The main difficulty consists in the nature of radical reactions in polypropylene since the majority of polypropylene macroradicals decay by β-scission and disproportionation. This leads to molecular weight decrease, branching the originally linear macromolecules, and an overall chemical change of polypropylene due to an increase of the double-bond concentration as well as of the amount of degradation and oxidation products.

Recombination of macroradicals proceeds simultaneously with the degradation process and can lead to crosslinking under certain conditions. The gel point can be reached using either a large amount of initiator when initiation by thermal decomposition of peroxide is employed[1] or a high dose when radicals are formed by irradiation.[2] Up to 80% of gel can be formed in polypropylene in such a way, but the properties of the polymer indicate that significant changes occur because of fragmentation of macroradicals.

The crosslinking efficiency can be increased by addition of a so-called coagent. Macroradical fragmentation is apparently retarded by coagent presumably because of macroradical addition to the reactive center of the coagent. A more stable radical is formed. The latter decays preferably by recombination with another radical or by transfer reaction. The effective coagents possess two or more active centers. A crossbond is formed if two reactive centers of the coagent molecule react with two different macroradicals. In such a case the link is actually identical with the coagent molecule.

Polyfunctional monomers are the most used coagents for polypropylene crosslinking. Divinyl benzene, diethylene glycol dimethacrylate, diallyl maleate, unsaturated esters and ethers of pentaerythritol, triallyl cyanurate, together with organic peroxides[3,4] or high-energy irradiation[5] have been used,

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to mention just a few of the wide scale of this kind of compounds. However, the efficiency of these coagents is not high enough especially at high additive concentration. Various side reactions mainly homopolymerization of coagent take place at higher additive amount.

Other compounds were searched for using as efficient coagents. About 80% of the gel was formed when a small amount of sulfur was added to organic peroxide.[6] Chloranil and its mixture with sulfur was found to be also an effective coagent. In this case it is even not necessary to use the radical initiator.[7] Acethylene[8] and a mixture of sulfur with terephthaloylchloride[9] were used in few cases. All these systems have a certain advantage but also serious hindrances, and polyfunctional monomers are preferred as the coagents.

p-Benzoquinone and bisphenol were described recently[10,11] to be highly effective coagents for polypropylene crosslinking. Some work has been done in the study of properties of crosslinked polypropylene by these systems.[12,13] In this article the systems consisting of organic peroxide and *p*-benzoquinone was investigated in detail from the point of view of efficiency of gel formation at polypropylene crosslinking.

EXPERIMENTAL

Unstabilized isotactic polypropylene Tatren HPF (Slovnaft, Czechoslovakia) has been used, its viscometric molecular weight being 220,000 g/mol. Dicumyl peroxide (Perkadox SB), benzoyl peroxide, and 1,4-ditertbutylperoxy diisopropyl benzene (Perkadox 14) were recrystallized from ethanol; *tert*-butyl perbenzoate (Fluka AG) and 2,5-dimethyl-2,5-ditertbutylperoxy hexyne (Luperox 130) were used without purification. The content of the peroxy groups was determined iodometricaly and was found to be higher than 95% of theoretical value. The coagent *p*-benzoquinone was used without purification.

Sample Preparation. The additives were added in the form of an acetone solution into a beaker with powdered polypropylene. After removing the solvent, slabs 0.5 mm thick were pressed at 20 MPa at temperatures of 170°C or higher. The gel content was calculated according to weight loss after 14 h extraction in boiling xylene.

RESULTS

The amount of gel formed vs. concentration of *p*-benzoquinone and *tert*-butyl perbenzoate is shown in Table I. The gel content increases with increasing peroxide amount unlike when changing the quinone concentration which shows maximum on the plot of gel content vs. quinone concentration.

Since polypropylene crosslinking is very sensitive to the temperature change,[14] the gel formation in dependence on temperature was investigated (Table II). At peroxide-initiated crosslinking of polypropylene, the rate of initiator decomposition is another very important parameter[1] besides initiator concentration and temperature. The decomposition rate of initiator influences the stationary concentration of radicals in the polymer and consequently also the ratio of recombination and fragmentation of macroradicals. This effect

TABLE I
Gel Content in Polypropylene at Various Concentrations of the Crosslinking System Components[a]

TBPB[b] (wt %)	Gel (wt %)							
1	0	47	68	77	50	—	—	—
2	0	62	84	82	79	58	2	0
3	0	71	92	93	96	93	68	—
4	12	74	84	94	94	90	67	59
5	—	82	94	99	99	—	—	—
Q[c] (wt %)	0	0.5	1.0	1.5	2.0	3.0	5.0	8.0

[a] Reaction temperature 170°C, time 5 min.
[b] TBPB = *tert*-butyl perbenzoate.
[c] Q = *p*-benzoquinone.

TABLE II
Polypropylene Gel Formation in Dependence on Temperature and Time of Reaction

TBPB[a] (wt %)	Q[b] (wt %)	Gel content (wt %)									
		170°C			190°C			220°C			258°C
2	1	74	84	79	86	82	74	84	69	72	—
2	2	39	79	81	89	80	85	80	88	86	85
2	5	0	2	21	4	7	12	33	59	49	46
4	1	73	84	70	81	79	76	82	74	74	57
4	2	57	94	86	78	88	89	80	92	95	—
4	5	32	67	79	69	75	75	59	79	79	85
Time (s)		60	300	720	20	60	180	5	20	60	10

[a] TBPB = *tert*butyl perbenzoate.
[b] Q = *p*-benzoquinone.

was investigated also in the presence of coagent. The crosslinking efficiency of various organic peroxides in polypropylene crosslinking is given in Table III.

DISCUSSION

The results indicate (Table I) that the amount of gel formed depends significantly on the concentration of peroxide as well as of coagent of crosslinking. Increasing the initiator concentration leads to the increase of gel content at any coagent concentration. The dependence of gel content on the benzoquinone amount shows a maximum. This maximum moves slightly to a higher concentration of the coagent when increasing the peroxide amount. The occurrence of the maximum can be explained considering the reaction of benzoquinone with radicals formed by peroxide decomposition. At high quinone concentration this process competes extensively with the reaction of initiator radicals with polypropylene decreasing the amount of initiating radicals. In

this case, presumably phenyl or methyl radicals formed by fragmentation of benzoyloxy or tertalkoxy radicals are the reacting species, more likely than primary radicals formed by peroxide decomposition.

It is surprising that the increase of *tert*-butyl perbenzoate concentration leads to just a slight shift of gel content maximum to high benzoquinone concentration. It means that comparatively small amount of quinone is consumed to form a network at a higher initiator concentration than at a lower one, even though a larger decay of quinone can be assumed at a higher peroxide concentration because of various side reactions. The experimental data may be explained by further reactions of quinone built in polymer network. Both π-bonds of two carbonyls as well as π-bonds between the carbons of benzoquinone can take part in the crosslinking reaction. For crosslinking, the addition of two macroradicals to one double bond is sufficient. Thus, also, the end macroradicals can be scavenged to polymer gel by addition to the quinone reactive center. These macroradicals cannot be direct precursors of crosslinked polypropylene in the absence of coagent. The end macroradicals are formed by fragmentation of random macroradicals as a competing reaction with the crossbond formation. The role of quinone as the coagent of crosslinking can consist in the ability of binding the fragments, i.e., the end macroradicals into a primary formed polymer network besides diminishing the fragmentation of macroradicals.

The effect of temperature on the crosslinking reaction is not so significant in the presence of benzoquinone unlike when polypropylene crosslinking is initiated by peroxide without coagent.[14] Several conclusions can be drawn from Table II, anyway. Maximum gel contents are practically independent on reaction temperature in the case when the ratio of quinone to peroxide is close to the optimal value. The prolonging time of the process causes the decrease of gel content to a certain extent. Increased temperature and prolonged

TABLE III
The Effect of Various Initiators and Time of Heating (Min) on the Amount of Gel (Wt %) Formed in Polypropylene at 170°C in the Presence of *p*-Benzoquinone

Peroxide (wt %)	Quinone (wt %)	L-101[a]		L-130[b]		BP[c]			DCP[d]		P-14[e]	
2	1	0	58	0	82	39	59	42	50	68	33	0
2	2	0	0	0	80	9	18	24	4	13	38	58
2	3	0	0	0	71	15	4	15	0	—	0	13
4	1	0	54	77	57	20	47	52	87	87	76	79
4	2	53	81	65	92	50	74	65	7	66	88	92
4	3	0	51	61	81	40	37	38	0	11	72	86
Time (min)		6	28	6	28	0.3	1	7	7	30	7	30

[a] L-101 = 2,5-ditertbutylperoxy-2,5-dimethyl hexyne.
[b] L-130 = 2,5-ditertbutylperoxy-2,5-dimethyl hexyne.
[c] BP = benzoyl peroxide.
[d] P-14 = 1,4-di-*tert*-butylperoxy diisopropyl benzene.
[e] DCP = dicumyl peroxide.

TABLE IV
The Efficiency e of Various Initiators According to Eq. (1)[a]

Peroxide	TBPB				L-101		L-130		DCP		P-14		BP	
Conc (wt %)	1	2	3	4	2	4	2	4	2	4	2	4	2	4
e	0.68	0.43	0.72	0.39	0.17	0.15	0.30	0.34	0.38	0.34	0.20	0.29	0.29	0.20
Quinone (wt %)	1.5	1	2	2	1	2	1	2	1	2	2	2	1	2

[a] The peroxide identification is the same as in Table II and III.

reaction time leads to enhancing the gel content if the quinone is overdosed. On the other hand, prolonged time of the process causes a slight decrease of the gel amount when reagents concentration is close to optimal. Apparently the *p*-benzoquinone behaves as a stabilizer of thermodegradation in this case. At high temperature and longer reaction time the degradation proceeds even after the initiator is completely decomposed. If quinone is present, it inhibits the degradation process and further crosslinking occurs. This is the case when concentration of the benzoquinone is higher than the optimal one. However, if the additives concentration ratio is about optimal at the beginning, the whole quinone amount will react parallelly with peroxide decomposition. Further heating leads to a decrease of gel content in such a case because of the thermal destruction similar to that of polypropylene crosslinked with peroxide without coagent.[14]

The effect of structure of various organic peroxides on crosslinking may be estimated from the data in Table III. The efficiency was calculated[15] according to equation

$$e = \frac{n}{[\mathrm{i}]} = \frac{1}{[\mathrm{i}]} \frac{10^3}{2M_n} \frac{1 - s^{0.5}}{s^{0.5} - s^{1.5}}$$

s being the soluble portion after extraction in boiling xylene, M_n the number average molecular weight determined from viscometric value, $M_v = 220{,}000$ g/mol, the estimated value of $M_w/M_n = 10$,[15] n is the concentration of crosslinks and [i] the concentration of the initiator (mol/kg). Table IV shows all calculated data for all peroxides used. Only the highest efficiency is given at all peroxide concentrations, i.e., when the optical ratio of peroxide and quinone as well as the optimal reaction time can be expected. The efficiency of crosslinking is shown to be much higher when compared with both the value about 0.05 for the system without coagent[14] or 0.12 that is the average crosslinking efficiency for comparable concentration of initiator when polyfunctional monomer was used as the coagent.[15] Various initiators exhibit different efficiencies. From this point of view they are ranked in accordance to the study of polypropylene crosslinking in the absence of coagent.[1] The conclusion can be made that in the presence of coagent the stationary level of macroradicals has a significant role, though not a decisive one as when crosslinking proceeds without coagent.

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