Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Efficiency of Chemical Cross-Linking of Polypropylene

E. Borsig[a]; A. Fiedlerová[a]; M. Lazár[a]
[a] Polymer Institute Slovak Academy of Sciences, Bratislava, Czechoslovakia

To cite this Article Borsig, E. , Fiedlerová, A. and Lazár, M.(1981) 'Efficiency of Chemical Cross-Linking of Polypropylene', Journal of Macromolecular Science, Part A, 16: 2, 513 — 528

To link to this Article: DOI: 10.1080/00222338108058488

URL: http://dx.doi.org/10.1080/00222338108058488

J. MACROMOL. SCI.–CHEM., A16(2), pp. 513-528 (1981)

Efficiency of Chemical Cross-Linking of Polypropylene

E. BORSIG, A. FIEDLEROVÁ, and M. LAZÁR

Polymer Institute
Slovak Academy of Sciences
809 34 Bratislava, Czechoslovakia

ABSTRACT

The efficiency of the chemical cross-linking of polypropylene was found to be dependent on the peroxide used (dicumyl peroxide, benzoyl peroxide, t-butyl peroxide, and t-butyl peroxybenzoate). The reason for different cross-linking efficiency of peroxide and enhancement of the cross-linking efficiency of peroxide in the presence of polyfunctional monomer-pentaerythritol tetrallyl ether are discussed.

INTRODUCTION

Small efficiency of the cross-linking of polypropylene was found a long time ago by studying the effect of ionizing radiation on hydrocarbon polymers [1]. This phenomenon has usually been explained by a theoretical view on simultaneous degradation and cross-linking of irradiated polypropylene. The ratio between degradation and cross-linking reactions is 0.4 for γ-irradiated atactic polypropylene and 0.8 for isotactic polypropylene [2]. The extent of the values of this ratio affects different molecular weight distribution of the samples used; at the same time this makes the accuracy of the portion determination of both processes doubtful. The value of the ratio for UV irradiated isotactic polypropylene with various kinds of sensitizers is 0.3 for S_2Cl_2 and 1 for 1,2,3,4,5,8-hexachloro-1,2,3,4-tetrahydronaphthalene [3]. As is seen, the proportion of the degradation reaction in polypropylene cross-linking is affected by many factors.

Chemical generation of radicals in polypropylene is accompanied by degradation and cross-linking [4]. Scission of polymer chains is expected at lower peroxide concentration (below 0.05 mol/kg dicumyl peroxide, 145°C, or below 0.03 mol/kg dibenzoyl peroxide, 73°C) and is accounted for by monomolecular degradation reaction. The cross-linking reaction starts to prevail over degradation at higher concentration of radicals with respect to its bimolecular character. This explanation is based on the idea of homogeneous spread of macroradicals in the system.

However, in the cross-linking of polyethylene, cross-links between macromolecules have been found to arise only in the presence of a suitable initiator which, by transfer reaction, gives rise to a pair of macroradicals in the place of its decomposition [5]. The more reactive the radicals that are produced by the initiator, the greater is the cross-linking efficiency. The cross-linking is initiated, e.g., by vinyl, phenyl, cyclopropyl, and primary alkyl radicals except for benzyl radical. Secondary and tertiary alkyl radicals are inefficient. If such a mechanism of the cross-linking is accepted for polypropylene, the theory for the course of cross-linking and degradation of this polymer should be modified [6].

The mechanism of degradation reaction of polypropylene is generally explained by fragmentation of tertiary alkyl macroradicals, while the cross-linking is explained by a combination of secondary alkyl macroradicals. The decreasing efficiency of peroxide cross-linking of copolymers of ethylene and propylene was accounted for in the same way [7].

The theories mentioned are rather simplified and they are not yet based on unambiguous measurements. For instance, only combination is assumed in the cross-linking of secondary alkyl radicals. Such behavior of alkyl radicals contradicts the properties of the low molecular weight alkyl radicals in the gaseous phase or in solution. Alkyl radicals not only dimerize (combine) but also considerably disproportionate. A question arises whether behavior of macroradicals in very viscous medium differs from that of the low-molecular weight radicals or whether the cross-linking mechanisms considered are not too simplified. Disproportion leads to a simultaneous decrease in the efficiency of cross-linking and in the significance of the fragmentation reaction of macroradicals. Seemingly, it is therefore useful to evaluate the portion of fragmentation reaction with respect to other possible reactions which decrease the cross-linking efficiency.

The aim of the present paper is to investigate the role of polyfunctional monomers (molecules containing several olefinic bonds) in raising the cross-linking efficiency of polypropylene. The problem has already been studied for several polymers and some coagents on the basis of polyfunctional monomers.

The majority of papers concentrate on aspects of the increase in the efficiency; however, the mechanism of the action of coagents is not clear.

In terms of one of theoretical views [9], a polyfunctional monomer polymerizes and cross-links in polypropylene to give a reactive network. The unchanged double bonds of the polymerized polyfunctional monomer are the sites for trapping macroradicals of polypropylene formed by ionizing radiation.

Sulfur is another type of effective coagent in chemical polypropylene cross-linking and is built in the polymeric network in the presence of peroxides [10]. At low molar ratio between sulfur and peroxide, monosulfide bridges are formed; as the ratio increases, the portion of polysulfide sulfur increases in cross-links. The favorable effect of sulfur on the increase of the cross-linking efficiency is accounted for by the reaction of macroradicals with sulfur and by an assumption that the radicals arising do not fragmentize [4]. The effect of polyfunctional monomers might also be explained in a similar way. Naturally, there are also other possible explanations but new experimental results are required for their study.

EXPERIMENTAL

Benzoyl peroxide was purified by precipitating with methanol from chloroform solution.

Dicumyl peroxide was recrystallized three times from undercooled ethanol.

Lauroyl peroxide (98%), t-butyl peroxybenzoate (98%), and di-t-butyl peroxide (99%) were used without further purification.

Pentaerythritol tetrallyl ether (PETA) was prepared from pentaerythritol and allyl bromide as described previously [11].

Isotactic polypropylene was an unstabilized polymer powder of the HP-F type (Slovnaft) having a molecular weight of 200,000. The samples of isotactic polypropylene were prepared by impregnating the polymer powder with additives added as a solution in chloroform. After solvent evaporation, the powder was mechanically homogenized and charged in glass ampules and finally sealed under nitrogen. The samples were annealed in a thermostated oil bath at 170 ± 0.1°C.

The gel content was determined by measuring the weight loss after extraction in xylene containing 0.1% hydroquinone for 36 h.

DETERMINATION OF THE RELATIVE CROSS-LINKING EFFICIENCY

The cross-linking efficiency was calculated as a molar ratio of cross-links formed and decomposed peroxide. The concentration of cross-links, n, was computed according to the relation [4]

$$n = \frac{10^3 \gamma}{2M_n} \qquad \text{mol/kg}$$

where γ is the degree of cross-linking and M_n is the number-average molecular weight of the polymer.

The degree of cross-linking was determined from the weight fraction, S, of a soluble polymer and in some cases from the gel point, i.e., from the minimum peroxide concentration at which the first portions of an insoluble polymer arise.

For calculating the degree of cross-linking, we used the equation

$$\gamma = \frac{1 - S^{0.5}}{S^{0.5} - S^{1.5}}$$

derived for the most probable molecular weight distribution [12]. This simple relation was chosen because of random degradation occurring in the polypropylene cross-linking, the most probable molecular weight distribution being thus formed from a rather polydisperse system.

With regard to the unknown form of the distribution function of the molecular weight of the polypropylene sample used, the cross-linking efficiency determined is of relative value. When employing relations valid for a wider distribution [13], the calculated absolute values of the cross-linking efficiency will be lower.

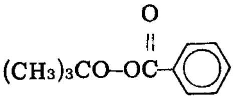
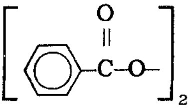
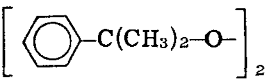
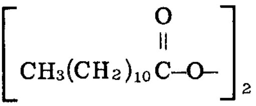
RESULTS AND DISCUSSION

Effect of the Type of Peroxide on the Cross-Linking Efficiency

The chemical initiation of the polypropylene cross-linking showed that the kind of initiator used determines the relative cross-linking efficiency (Table 1).

The observed independence of the cross-linking efficiency of the rate of the initiator decomposition might indicate that the competitive reactions of termination and fragmentation of macroradicals are not determining for the process of cross-linking. If in chemical cross-linking no other factors were applied, a correlation should be expected between immediate concentration of macroradicals (i.e., the rate of radical formation) in the system and the number of cross-links. With the increasing stationary concentration of radicals, the bimolecular termination ought to be applied to the detriment of macromolecular fragmentation. As a result, we might expect a rise in the cross-linking efficiency with an increase in the rate of peroxide decomposition.

TABLE 1. Cross-linking of Isotactic Polypropylene (PP) by Organic Peroxides with Various Half-Lives of Decomposition ($\tau/2$); Gel Content in %, Relative Efficiency of Cross-Linking (R.E.). (Temperature of the reaction was 170°C and time of the reaction was six half-lives of the appropriate initiator.)

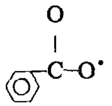
Peroxides	$\tau/2$ (s)	Concentration of peroxide (mol/kg PP)	Gel %	R.E.
	57	0.41	63	0.061
	2	0.42	42	0.045
	230	0.56	46	0.034
 $[CH_3(CH_2)_{10}C(=O)-O-]_2$	0.4	0.50	0	0.000
$[(CH_3)_3C-O-]_2$	340	1.37[a]	0	0.000

[a] Cross-linking was not observed at a lower peroxide concentration.

The situation is, in fact, more complicated, and differences in efficiency are probably connected with the different reactivities of the radicals arising from the peroxides used. One can imagine that the more reactive radicals will give macroradicals closer to one another than the less reactive radicals. The closer the pair of macroradicals, the more probable will be the formation of the cross-link competing with fragmentation reaction.

Looking at the structure of peroxides, it seems that the most efficient of the cross-linking initiators are those released by their decomposition benzoyloxy or phenyl radicals. On the contrary, initiators giving alkyl radicals are inefficient. This is the case with lauroyl peroxide which decomposes into 11 carbon primary alkyl radicals releasing CO_2 simultaneously [14]. A similar situation arises by the decomposition of di-t-butyl peroxide. In the presence of cyclohexane as much as 30% of the original t-butoxy radicals decompose into methyl radicals and acetone at 170°C [15]. It should be noted that two propylene units in a polypropylene chain have almost the same reactivity as cyclohexane. Fragmentation of cumyloxy radicals is still greater. Under the experimental conditions of cross-linking, 83% [15] or 90% [16] of primary radicals are decomposed. In the case of cumyloxy radicals, fragmentation to phenyl radical and acetone will also be probable to a certain extent. Phenyl radicals are also formed in polypropylene by decomposition of benzoyloxy radicals ($k_{170°C}$ extrapolated = 1.4×10^{-6} s^{-1}) [15].

In order to find out whether the assumption of the effect of the reactivity of primary radicals on the cross-linking efficiency is real, we shall try to quantify the reactivity of the radicals considered. The rate constants for the transfer reaction of radicals with toluene at 170°C are taken as a measure of the reactivity [14]. The reactivity of the methyl of toluene hydrogen is regarded as almost identical with that of one propylene unit of the polypropylene chain. The range of the reactivity for the rate constants of the respective radicals is relatively wide, and the corresponding relative distances, d, which the radicals pass from the site of formation to the place of reaction are:

	$\dot{C}H_3$	$(CH_3)_3CO^{\bullet}$		
k ($dm^3mol^{-1}s^{-1}$)	5×10^3	9×10^4	1×10^6	1×10^7
d	45	10	3	1

The relative distance d of primary radicals is given by the square root of the ratio of the rate constants of transfer reaction. (Here we used relation for particle diffusion $d^2 = 6Dt$.) In orientation, calculation of the same diffusion coefficient, D, was considered; the relative time, t, of the existence of the radical is determined by the ratio of the rate constants for transfer reaction. If the diffusion coefficient is also taken into account, the relative distances, d, between methyl and phenyl radicals will be still greater.

At the same time it should be noted that the comparison of distances of radicals is not as illustrative as changes in local concentration arising by diffusion of radicals. Concentrations of the respective radicals are indirectly proportional to the third root of the distance where the primary radicals are diffused before transfer reaction. Comparison of the local concentration of phenyl and methyl radicals gives a difference of about 5 orders of magnitude, which is significant for the competition between termination and fragmentation reactions.

On this basis an assumption of different efficiency of the cross-linking by initiators producing radicals of different reactivities seems to be justified (Table 1). Benzoyl peroxide is seemingly not suitable for this assumption because its efficiency is smaller than that of t-butyl peroxybenzoate. Here, however, account has to be taken of a large portion of induced decomposition of benzoyl peroxide at which radicals of the decomposing peroxide or radicals of the medium decompose peroxide. Obviously, this peroxide decomposition is inefficient for cross-linking. For illustration, it can be said that in the decomposition in atactic polypropylene at 80° C, the ratio between spontaneous and induced decomposition (S/i) depends on the peroxide concentration [17]:

BP,	mol/kg PP	0.01	0.1	0.4
S/i		10.9	1.1	0.27

Induced decomposition is not as significant in t-butyl peroxybenzoate as in benzoyl peroxide [18].

The great difference between the efficiencies of di-t-butyl peroxide and dicumyl peroxide is probably connected with the fragmentation of primary cumyloxy radicals to reactive phenyl radicals and with a diffusion rate of cumyloxy radicals lower than that of t-butyloxy radicals. These differences between the properties of primary radicals will be reflected in the formation of a pair of macroradicals in closer vicinity in the case of dicumyl peroxide; this will support production of cross-links between macromolecules.

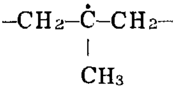
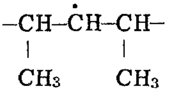
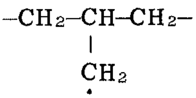
Greater reactivity of radicals can also increase the cross-linking efficiency as a result of smaller selectivity of the attack of the polypropylene chain. This can lead to a larger grouping of secondary and primary alkyl macroradicals which, in termination, combine more than they disproportionate.

Causes of Small Cross-Linking Efficiency of Polypropylene

The difficulties encountered in polypropylene cross-linking can also follow from a high portion of disproportion and fragmentation of polypropylene macroradicals.

The influence of disproportion on the cross-linking efficiency can be depicted on the basis of the analysis of the reaction products in termination of the low-molecular weight radicals of various structures. The measurements performed so far show [14] that the ratio of the rate constants for disproportion, k_d, and the rate constant for combination, k_c, depends on the number of hydrogens in the β-position with respect to the carbon atom with an unpaired electron, on the reactivity of the alkyl radical, and on the hydrogen atoms abstracted. The ratio k_d/k_c is little dependent on temperature and on the fact

TABLE 2. Calculated Values of the Ratio k_d/k_c of Polypropylene Macroradicals, Their Representation, and Their Cross-Linking Efficiencies

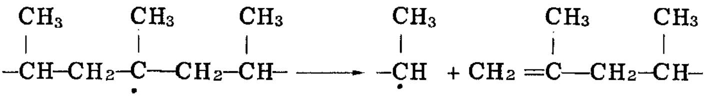
Radical	k_d/k_c	Occurrence (%)		Cross-linking efficiency
		a	b	
 $-CH_2-\underset{\underset{CH_3}{\vert}}{\dot{C}}-CH_2-$	2.9	17	54	0.26
 $-\underset{\underset{CH_3}{\vert}}{CH}-\dot{C}H-\underset{\underset{CH_3}{\vert}}{CH}-$	0.6	33	43	0.62
 $-CH_2-\underset{\underset{\dot{C}H_2}{\vert}}{CH}-CH_2-$	0.08	50	3	0.93

[a] At nonselective attack of polypropylene chain.

[b] At selective attack of primary, secondary, and tertiary hydrogen, ratio 1:10:50.

whether the termination reaction is performed in the gas or liquid phase. Because of numerous and repeated measurements, the ratio k_d/k_c can also be estimated relatively precisely for macroradicals of polypropylene (Table 2). The average value of the ratio k_d/k_c in the polypropylene sample depends on the representation of individual types of macroradicals in the polymer. The value of the cross-linking efficiency is assigned to the types of macroradicals mentioned without considering the fragmentation reaction.

With respect to the selectivity of primary radicals and subsequent transfer reactions of the more reactive alkyl macroradicals to polypropylene, tertiary or secondary alkyl radicals were mainly considered as basic radicals. The value of k_d/k_c in the termination reaction of these two radicals is 1.5 and the cross-linking efficiency is 0.4. Even at the highest value of k_d/k_c, i.e., when only alkyl macroradicals take part in the cross-linking reaction, the cross-linking efficiency of polypropylene should not be so low. In the case indicated, the efficiency would be about 4 times greater than the highest experimental value observed by us (Table 1). Another reason for the low cross-linking efficiency of polypropylene, which has often been a subject of discussion, is the fragmentation of macroradicals which causes the original molecular weight of the polymer chain to decrease:



$$-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{\bullet}{C}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}- \longrightarrow -\overset{CH_3}{\overset{|}{\underset{\bullet}{C}H}} + CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-$$

The study of the fragmentation of radicals undertaken so far does not give a more precise estimate of the rate constants for fragmentation of polypropylene macroradicals.

Alkyl radicals with a small numer of atoms fragmentize by β-scission of the C–C bond with the rate constant [14].

$$k = 10^{14.1\pm0.5} \exp - \frac{134 \pm 17 \text{ (kJ/mol)}}{RT} \quad [s^{-1}]$$

i.e., the rate constant can range between 7×10^{-5} and $5\ s^{-1}$ for a temperature of 170° C. Fragmentation with the lowest rate constant cannot compete seriously with termination. If the fragmentation should be applied under these conditions, the stationary concentration of radicals would have to decrease below 10^{-10} mol/kg:

$$\frac{\text{rate of fragmentation}}{\text{rate of termination}} = \frac{k_f R}{k_t R^2} = \frac{7 \times 10^{-5}}{10^6 R}$$

Such a low value of the stationary concentration of macroradicals is not probable at rapid peroxide decomposition. Fragmentation becomes real for the highest value of the rate constant for fragmentation.

The presence of the fragmentation reaction in polypropylene at a temperature higher than 100° C can be assumed because it is known that by illumination of polypropylene with UV light in vacuum, an increase in molecular weight of the polymer is observed below 100° C and above 100°C the molecular weight decreases [19].

In view of the cross-linking process the fragmentation reaction is a serious obstacle mainly because it is strengthened by the chain character of this reaction. The decay of a macroradical is accompanied by the formation of a primary alkyl radical, leading through transfer reaction mainly to tertiary macroradical with the possibility of the repetition of the fragmentation reaction. The cycle of the chain process can be repeated several times. The smaller the concentration of radicals, whether total or local in the range of the formation of a pair of radicals, the greater will be the number of iterations of the cycle.

TABLE 3. The Content of Insoluble Polymer (% gel) and Cross-Linking Efficiency with PETA (0.24 mol/kg) and Dicumyl Peroxide (DCP) or Di-t-butyl Peroxide (DTBP)

Temperature and time of cross-linking	0.19 mol/kg DCP		0.34 mol/kg DTBP	
	% gel	Efficiency	% gel	Efficiency
150°C, 2 h	56[a]	0.121	1.2[c]	0.037
180°C, 15 min	65[b]	0.138	7.8[d]	0.038

The number of half-lives of peroxide decomposition: [a] 6; [b] 14; [c] 2.8; [d] 6.

The end radical being formed in the fragmentation reaction of tertiary or secondary macroradical can also combine with original macroradicals and thus form the branched structure. This reaction increases the molecular weight of the polymer and the probability of cross-linking.

Increase of the Cross-Linking Efficiency by Coagents

By starting from the highest value of the rate constant for the fragmentation of alkyl radicals and the current value of the addition reaction of alkyl radicals to olefinic bonds, one can expect competition of both reactions in the presence of a polyfunctional monomer. The fragmentation reaction is probably not eliminated completely because the radical formed by addition can again produce by transfer reaction a labile alkyl macroradical which is able to fragmentize. Polyfunctional monomer grafted to polypropylene is an active site for trapping another macroradical and for the formation of a cross-linked structure by connecting the macromolecules. This alternative was verified by cross-linking in the presence of pentaerythritol tetrallyl ether (Table 3) which was found to increase the cross-linking efficiency 3 times in comparison with the cross-linking by dicumyl peroxide alone.

The different efficiency of the two initiators shows that the rate of attack of polypropylene by primary radicals is higher than the addition of these radicals to a polyfunctional monomer. Radicals of the polyfunctional monomer can also play a role in the enhancement of cross-linking efficiency with di-t-butyl peroxide.

Seemingly the cross-linking efficiency increases with increasing concentration of polyfunctional monomer only to 3-4%; above this value, no changes are observed in the gel content (Fig. 1). This is due to the large fraction of the low molecular polypropylene, and

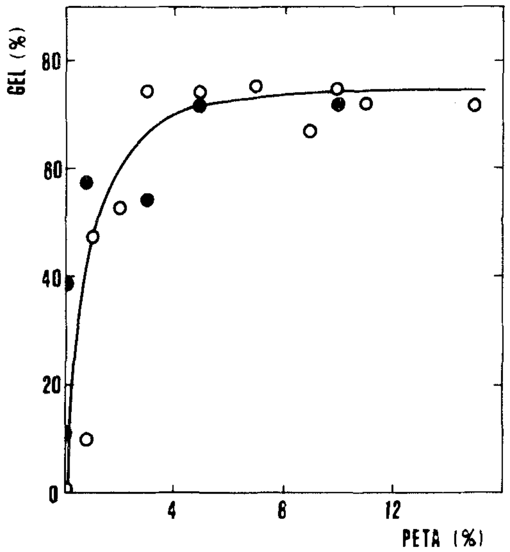


FIG. 1. A plot of the gel content in cross-linked polypropylene against the amount of pentaerythritol tetrallyl ether (PETA) in the presence of 3% t-butyl peroxybenzoate (•) and 5% dicumyl peroxide (○).

therefore a rise in the gel content above 70-80% requires a relatively great increase of the efficiency, its occasional changes being overlapped by experimental imprecisions. A comparison of the course of cross-linking containing 1.5% PETA (Fig. 2) with that containing 10% PETA shows that the cross-linking efficiency varies with the content of the polyfunctional monomer (Table 4).

A relatively high cross-linking efficiency at the gel point containing 10% pentaerythritol tetrallyl ether is connected with the polymerization of grafted residues of the polyfunctional monomer. In addition, suppression of the fragmentation of macroradicals has to be taken into account.

A similar relative rise in the cross-linking efficiency also occurs when using t-butyl peroxybenzoate as the source of radicals (Fig. 3). The cross-linking efficiency is higher as compared with the cross-linking of dicumyl peroxide, showing that the primary radicals react preferentially with polypropylene and not with the polyfunctional monomer. This situation will arise especially at low concentrations of pentaerythritol tetrallyl ether.

The evalutation of the results of the cross-linking (Fig. 3) in terms of the modified relation of Charlesby and Pinner [20]:

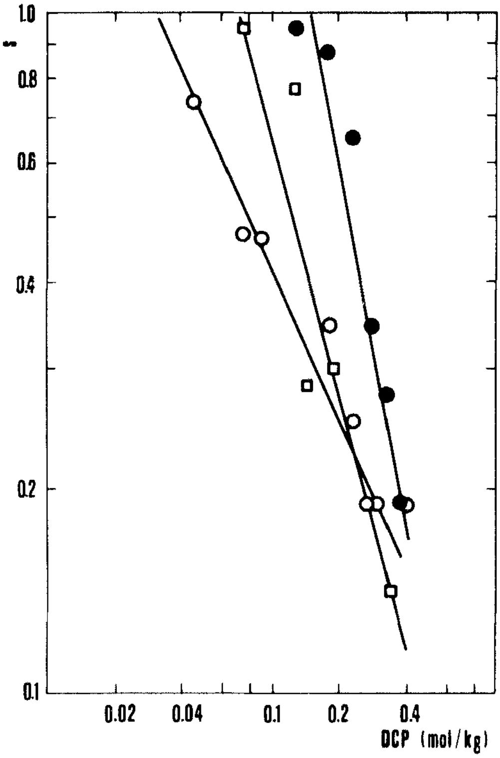


FIG. 2. Logarithmic dependence of the amount of the soluble portion of polypropylene on the dicumyl peroxide concentration in the presence of PETA: (●) 1%, (□) 5%, (○) 10%.

TABLE 4. Cross-Linking Efficiency of Polypropylene as a Function of the Gel Content (or of DCP content, see Fig. 2) in the Presence of Different Amounts of Pentaerythritol Tetrallyl Ether (PETA)

	Cross-linking efficiency		
% PETA	At gel point	At 50% gel	At 80% gel
1	0.09	0.10	0.09
5	0.19	0.18	0.13
10	0.42	0.28	0.13

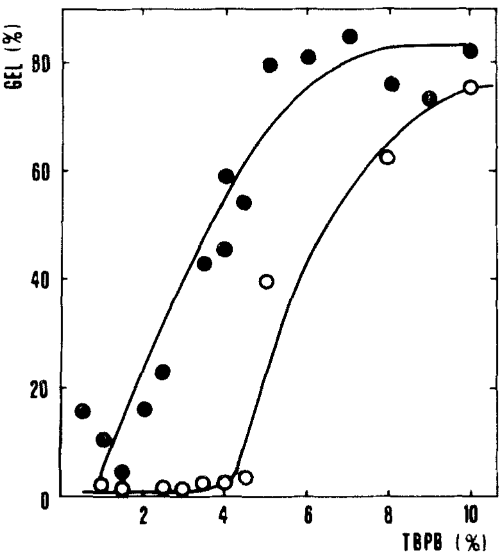


FIG. 3. Effect of PETA (1%) on the gel content in cross-linked polypropylene as a function of the amount of t-butyl peroxybenzoate: (○) without PETA, (●) with 1% PETA.

$$s + s^{0.5} + \frac{p}{q} + \frac{k}{TBPB}$$

where s is the soluble portion of the cross-linked polymer, p/q is the ratio between degradation and cross-linking reaction, k is a constant, and TBPB is the concentration of t-butyl peroxybenzoate, yields p/q = 0.3. The dependence is not linear over the whole range of the inversion values for t-butyl peroxybenzoate concentration. The value of p/q was obtained by extrapolating the data to the highest peroxide concentration k/TBPB = 0. The values of the sum $s + s^{0.5}$ near the gel point or for concentrations of t-butyl peroxybenzoate lower than 2.5% are not linear. In this region of peroxide concentrations the greatest differences occur between the relations for pure t-butyl peroxybenzoate and a mixture with pentaerythritol tetrallyl ether.

In the evaluation of the results of dicumyl peroxide cross-linking, a deviation from linearity occurs at peroxide concentrations lower than 5%. The effect of the concentration of pentaerythritol tetrallyl ether on the value of p/q cannot be evaluated unambiguously from the results of cross-linking by both peroxides.

The effect of pentaerythritol tetrallyl ether on the course of

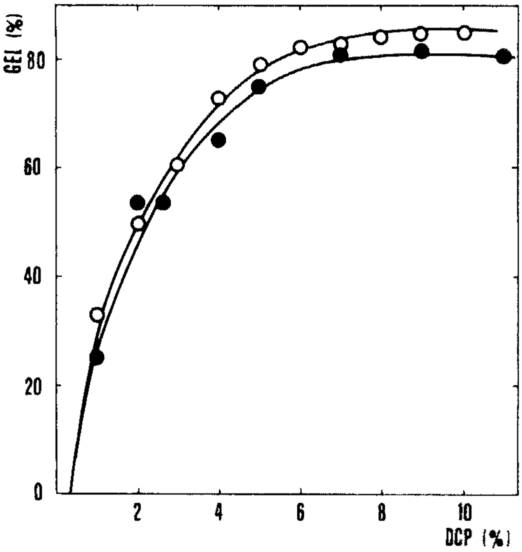


FIG. 4. Comparison of a plot of the gel content versus dicumyl peroxide concentration in the presence of 10% PETA (●) with a similar plot; polypropylene contained besides dicumyl peroxide and PETA di-t-butyl peroxide (○). The amount of di-t-butyl peroxide varied with changing dicumyl peroxide concentration so as to obtain the total content of 10% of both peroxides in each sample.

cross-linking was verified by employing a mixture of initiators: effective (dicumyl peroxide) and ineffective (di-t-butyl peroxide). On the basis of the identical course of the dependence of the gel content on dicumyl peroxide concentration in polypropylene either of pure DCP or in the presence of di-t-butyl peroxide (Fig. 4), we can conclude that the secondary radicals arising by addition of the primary radicals to polyfunctional allyl monomer do not produce polypropylene radicals (by transfer reaction). At the same time, the primary radicals from di-t-butyl peroxide probably react preferentially with polyfunctional monomer; this decreases the degradation of polypropylene and thus no drop in the gel content is observed in the presence of this initiator in comparison with pure DCP.

The effect of polyfunctional monomer on the enhancement in the cross-linking efficiency of polypropylene is probably caused by addition of a monomer to macroradicals of polypropylene. On repeating this reaction with polyfunctional monomer grafted to polypropylene, a branched, almost cross-linked polymer structure is formed. Besides the repeated addition reaction, a transfer reaction can also play a role. In this case the grafted monomers give allyl radicals combining almost exclusively in the termination reaction (k_d/k_c = 0.008), which increases the cross-linking efficiency.

CONCLUSION

The choice of the source of radicals and a suitable admixture which decreases the portion of the chain fragmentation of macroradicals is important for the solution of the problem of polypropylene cross-linking.

A source of reactive radicals is necessary for the formation of a pair of macroradicals of polypropylene at the smallest distance from the decay of initiator so that the mutual reaction of radicals would efficiently compete with intermolecular transfer reaction where the distance among radical centers will increase. The increase in the distance among macroradicals reduces the portion of the cross-linking reaction to the detriment of macroradical fragmentation.

Macroradicals separating due to the intermolecular transfer reaction can produce a cross-link on meeting another radical. Regarding the monomolecular character of fragmentation reaction, the high radical concentration can be helpful for cross-linking. However, this does not appear to be of prime importance.

An admixture able to react with labile macroradical of polypropylene will increase the cross-linking efficiency before its fragmentation. The admixtures probably take place in several chemical reactions. The simplest action of the admixture in the cross-linking process is the bonding of polypropylene macroradicals by addition reaction.

The polypropylene macroradical can be protected from fragmentation not only by addition but also by transfer reaction with an admixture giving an inactive (allyl) radical of the admixture. Such a radical then combines with another macroradical and protects it from fragmentation; moreover, it creates an active place for another cross-linking reaction.

The effect of a polyfunctional monomer or, more generally, of an admixture on the cross-linking of polypropylene can be many-sided, the cross-linking efficiency being dependent on the kind of admixture. The proper choice of admixtures requires a more detailed understanding of the cross-linking process and of the competitive reactions of polypropylene macroradicals.

REFERENCES

[1] R. M. Black and B. J. Lyons, Nature, 180, 1346 (1957); Proc. R. Soc. London, A, 253, 322 (1959). F. B. Waddington, J. Polym. Sci., 31, 221 (1958). H. Solne and Y. Tazima, Nature, 188, 315 (1960). R. P. Gupta, Kolloid Z., 174, 74 (1961); J. Phys. Chem., 66, 849 (1962).

[2] W. Schnabel and M. Dole, J. Phys. Chem., 67, 295 (1963).

[3] H. Wilski, Kolloid.-Z. Z. Polym., 188, 4 (1963).

[4] R. Rado, Premenné reakcie polymérov budené peroxidmi (Transfer Reactions of Polymers Initiated by Peroxides), Alfa, Bratislava, 1970, pp. 131, 133.

[5] G. W. Van Dine and R. G. Shaw, Polym. Prepr., 12(2), 713 (1971).

[6] I. Chodák, K. Fabianová, E. Borsig, and M. Lazár, Angew. Makromol. Chem., 69, 107 (1978).

[7] L. D. Loan, J. Polym. Sci., Part A, 2, 3053 (1964).

[8] G. Odian and B. S. Bernstein, Nucleonics, 80 (1963).

[9] G. Odian and B. S. Bernstein, J. Polym. Sci., Part A, 2, 2835 (1964).

[10] C. G. Moore and B. R. Frego, J. Appl. Polym. Sci., 8, 1957 (1964).

[11] P. L. Nichols and J. R. E. Janovsky, J. Am. Chem. Soc., 67, 46 (1945).

[12] A. Charlesby, Proc. R. Soc., London, 222, 542 (1954); Atomics, 5, 12 (1954); J. Polym. Sci., 11, 513 (1953). S. H. Pinner, Proc. R. Soc., London, A, 249, 367 (1959).

[13] M. L. Miller, The Structure of Polymers, Reinhold, New York, 1966, p. 318.

[14] J. K. Kochi, (ed.), Free Radicals, Vol. 1, Wiley-Interscience, New York, 1973, pp. 30, 51, 74, 251.

[15] J. K. Kochi (ed.), Free Radicals, Vol. 2, Wiley-Interscience, New York, 1973, pp. 684, 698.

[16] I. Chodák and D. Bakoš, Collect. Czech. Chem. Commun., 43, 2574 (1978).

[17] R. Rado, D. Šimunková, and L. Malak, Vysokomol. Soedin., 4, 304 (1962).

[18] D. Swern (ed.), Organic Peroxides, Vol. 1, Wiley-Interscience, New York, 1970, p. 276.

[19] N. Grassie and W. B. H. Leeming, Eur. Polym. J., 11, 809 (1975).

[20] A. Charlesby and S. H. Pinner, Proc. R. Soc., London, A, 249, 367 (1959).

Accepted by editor October 26, 1979
Received for publication March 5, 1980