Crosslinking of Polyethylene by Dicumyl Peroxide in the Presence of 2,4-Diphenyl-4-methyl-1-pentene

Shuji Suyama,[†] Hideyo Ishigaki, Yasumasa Watanabe, and Tomoyuki Nakamura

Fine Chemicals & Polymers Research Laboratory, NOF Corporation, Taketoyo-cho, Chita-gun, Aichi 470-23, Japan

ABSTRACT: Crosslinkings of low density polyethylene, high density polyethylene, and ethylene propylene rubber were carried out using dicumyl peroxide as a crosslinking agent. The addition of 2,4-diphenyl-4-methyl-1-pentene (α-methylstyrene dimer: MSD) as a coagent increased the scorch time at 145°C as well as the crosslinking efficiency at 180°C. The scorch inhibition mechanism is explained by the addition-fragmentation reaction between MSD and polymer radicals. A reaction mechanism for the production of highly crosslinked polymers is postulated and discussed.
KEY WORDS   Crosslinking / Polyethylene / Scorch / α-Methylstyrene Dimer / Addition-Fragmentation /

The crosslinking of polyolefins such as polyethylene (PE) and ethylene propylene rubber (EPR) is conveniently achieved by the use of organic peroxides such as dicumyl peroxide (DCP) as crosslinking agent. The efficiency of the peroxide-initiated crosslinking can be greatly increased by the addition of coagents (crosslinking activators) such as triallyl cyanurate, triallyl isocyanurate, quinone dioxime, diallyl phthalate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, N,N'-m-phenylenebismaleimide, 1,2-polybutadiene and so on.[1-5]

In addition to increasing the crosslinking efficiency, it is also important to prevent premature crosslinking which may occur during the pre-crosslinking process. The premature crosslinking is commonly referred to as scorch. It was reported that nitrites,[6] 2-mercaptobenzothiazole,[7] and hydroquinones[8] act as effective scorch inhibitors for PE crosslinking.

It is very useful and practical to achieve to increase crosslinking efficiency and to inhibit scorch at the same time simply by adding a single compound. Recently, we have shown that 2,4-diphenyl-4-methyl-1-pentene (α-methylstyrene dimer: MSD) undergoes chain transfer through a free radical addition-fragmentation reaction in styrene polymerization.[9] If the addition-fragmentation reaction occurs even in the case of polyolefin crosslinking, the addition of MSD to a crosslinking system will significantly influence the crosslinking behavior.

In this paper, we report on the excellent effects of MSD on the crosslinking of low density polyethylene (LDPE), high density polyethylene (HDPE), and ethylene propylene rubber (EPR) and present a possible action mechanism of MSD for PE crosslinking.

EXPERIMENTAL

Materials

Commercially available DCP (NOF Corporation), MSD (NOF Corporation), and other additives were used without further purification. LDPE was available from Nippon

---

† To whom all correspondence should be addressed.

Unicar Co., Ltd. (NUC-9025) and HDPE from Ace Polymer Co., Ltd. (HDF6080V). EPR was supplied from Japan Synthetic Rubber Co., Ltd. (EP02P), containing 26 wt% of propylene unit.

Crosslinking test

Polyethylene, DCP, and the additive were kneaded with a hot roll at around 110°C for about 20 minutes. The resulting blend was subjected to crosslinking tests at 145 and 180°C using JSR Curelastometer III. The scorch time at 145°C and the maximum torque value at 180°C were obtained from the time–torque relationship.

RESULTS

Crosslinking of LDPE

The crosslinking of LDPE were carried out using DCP as a crosslinking agent in the presence or absence of MSD at 145 and 180°C. The representative time–torque relationships, as obtained by a curelastometer, are depicted in Figure 1. It is apparent that torque increased more mildly at 145°C, while increased more rapidly at 180°C when MSD was added. To our surprise, the maximum torque value at 180°C was increased by a factor of 1.5 by the addition of MSD. These results clearly demonstrate that MSD acts as a retarder at 145°C and an activator at 180°C for LDPE crosslinking.

The effect of addition of other compounds, including already known coagents or scorch inhibitors, was also examined. From the time–torque relationships obtained by LDPE crosslinking in the presence of these additives, the maximum torque value at 180°C and the scorch time at 145°C were determined for each compound (Table I). Here, scorch time denotes the time taken to reach 10% of the maximum torque value. That is, the longer scorch time shows the better result. The addition of triallyl isocyanurate (run 3), 1,2-polybutadiene (run 4), ethylene glycol dimethacrylate (run 5),
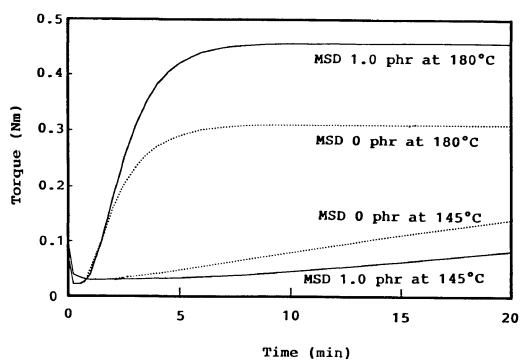

Figure 1. Effect of MSD on LDPE crosslinking by DCP at 145 and 180°C: DCP, 2.5 phr.

Table I. Effect of additives on LDPE crosslinking by DCP[a]

| Run additive[b] | Max. torque[c] | Scorch time[d] |
	Nm	min
1 None	0.30	5.5
2 MSD	0.45	17.0
3 Triallyl isocyanurate	0.44	2.6
4 1,2-Polybutadiene	0.41	7.0
5 Ethylene glycol dimethacrylate	0.40	8.7
6 N,N'-m-Phenylene bismaleimide	0.35	2.0
7 Trimethylolpropane trimethacrylate	0.35	6.7
8 2,6-Di-*t*-butyl *p*-cresol	0.28	9.0
9 *n*-Octyl methacrylate	0.26	9.3
10 N-Nitrosodiphenyl amine	0.18	16.4
11 2-Mercaptobenzo thiazole	0.095	25.0

[a] DCP concentration, 2.5 phr. [b] Additive concentration, 1.0 phr. [c] Maximum torque value at 180°C. [d] Scorch time at 145°C.

N,N'-m-phenylenebismaleimide (run 6), and trimethylolpropane trimethacrylate (run 7) was effective in increasing the maximum torque value, but had little or a negative effect on increasing the scorch time. On the other hand, the addition of 2,6-di-*t*-butyl-*p*-cresol (run 8), *n*-octyl methacrylate (run 9), N-nitrosodiphenylamine (run 10), and 2-mercaptobenzothiazole (run 11) increased the scorch time, but

372

Table II. Effect of MSD concentration on LDPE
crosslinking by DCP[a]

MSD	Max. torque[b]	Scorch time[c]
phr	Nm	min
0	0.30	5.5
0.25	0.34	9.3
0.50	0.41	14.0
1.0	0.45	17.0
2.0	0.31	16.0

[a] DCP concentration, 2.5 phr. [b] Maximum torque value
at 180°C. [c] Scorch time at 145°C.

Table III. Effect of MSD concentration on
HDPE crosslinking by DCP[a]

MSD	Max. torque[b]	Scorch time[c]
phr	Nm	min
0	0.37	6.3
0.5	0.66	8.0
1.0	0.67	11.4
1.5	0.65	11.6
2.0	0.62	11.4

[a] DCP concentration, 2.5 phr. [b] Maximum torque value
at 180°C. [c] Scorch time at 145°C.

reduced the maximum torque value. As seen
in the table, MSD (run 2) is the best additive
of all tested here because only MSD could
increase both the scorch time and the maximum
torque value.

The effect of MSD concentration on LDPE
crosslinking is shown in Table II. When the
concentration of DCP was fixed at 2.5 phr
(parts per hundred parts of resin), the optimum
concentration of MSD was found to be around
1.0 phr. More addition than 1.0 phr caused a
decrease of the maximum torque value.

Crosslinking of HDPE and EPR

The effect of MSD on HDPE crosslinking
was also examined. The maximum torque
values and the scorch times at various con-
centrations of MSD are shown in Table III.
It is clear that MSD is effective in increasing
the scorch time as well as the maximum torque

Table IV. Effect of MSD concentration on
EPR crosslinking by DCP[a]

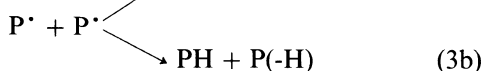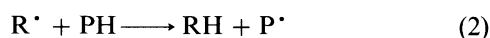| MSD	Max. torque[b]	Scorch time[c]
phr	Nm	min
0	1.06	6.0
0.25	1.10	9.0
0.50	1.11	7.0
0.75	1.11	27.0

[a] DCP concentration, 2.5 phr. [b] Maximum torque value
at 180°C. [c] Scorch time at 145°C.

value. The optimum concentration of MSD
was around 1.0 phr when 2.5 phr of DCP was
used. For example, the addition of 1.0 phr of
MSD resulted in an increase of the maximum
torque value of about 80%.

Finally, we investigated the effect of MSD
on EPR crosslinking (Table IV). Although
MSD had little effect on increasing the
maximum torque value, the addition of MSD
(*e.g.*, 0.75 phr) greatly increased the scorch
time.

DISCUSSION

The crosslinking of PE by organic perox-
ides is induced by homolytic decomposition of
organic peroxides (eq 1). Active free radicals
($R^\cdot$) produced from peroxides abstract hydro-
gen atoms from the polymer backbone to give
polymer radicals (eq 2). When any additives
are not present, the polymer radicals ($P^\cdot$) react
with other polymer radicals through combina-
tion (eq 3a) or disproportionation (eq 3b). The
crosslinking efficiency is decreased by the
disproportionation reaction.

$$\text{Peroxide} \longrightarrow 2R^\cdot \qquad (1)$$

$$R^\cdot + PH \longrightarrow RH + P^\cdot \qquad (2)$$

$$P^\cdot + P^\cdot \underset{\searrow\ PH + P(\text{-}H)}{\overset{\nearrow\ P\text{-}P}{}} \qquad \begin{matrix}(3a)\\[1em](3b)\end{matrix}$$

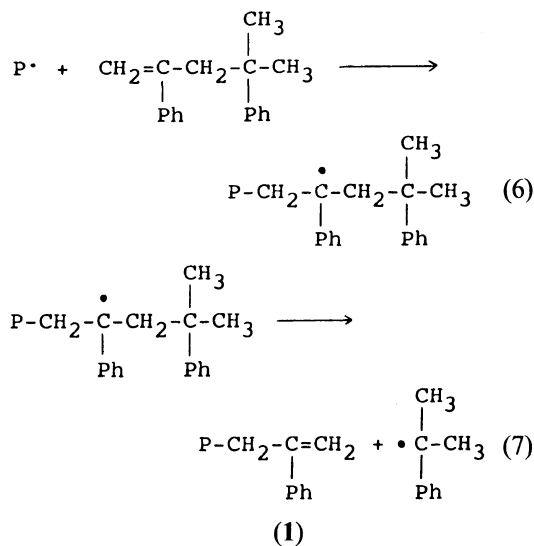When the polymer (PH) is PE, P$\cdot$ are mainly secondary alkyl radicals. It was reported that the ratio of disproportionation to combination for the isopropyl radical (a simple secondary alkyl radical) is 1.2.[10] Thus, it is assumed that about half of the polymer radicals undergo the disproportionation reaction when PE crosslinking is carried out using only a peroxide initiator (*i.e.*, in the absence of coagents). To increase crosslinking efficiency, we need to suppress such a disproportionation reaction using a suitable coagent. On the contrary, the combination reaction (eq 3a) becomes an unfavorable reaction during the pre-crosslinking process since it causes a scorch problem. Therefore, it is also necessary to suppress the combination reaction during the pre-crosslinking process.

It is well known that MSD is an effective chain transfer agent for styrene polymerization.[9,11] Recently, we have reported that MSD undergoes chain transfer through a free radical addition-fragmentation reaction in styrene polymerization.[9] That is, propagating polymer radicals add to the double bond of MSD to give intermediate adduct radicals (eq 4), and then the adduct radicals undergo fragmentation to expel cumyl radicals (eq 5). The similar addition-fragmentation
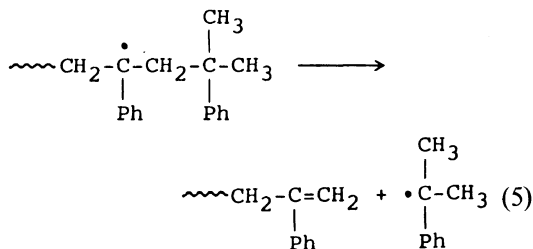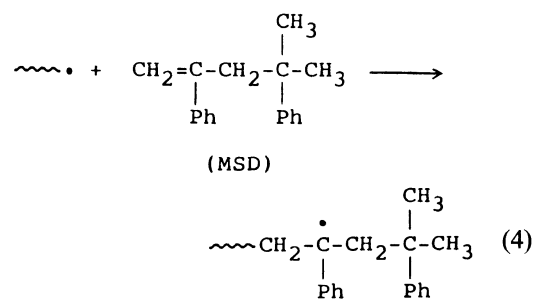
reaction will occur even in the present case since addition of alkyl radicals to the styrenic double bond is a facile reaction. For example, the absolute rate constant for addition of the 5-hexenyl radical to styrene was reported to be around $10^5 \, M^{-1}s^{-1}$.[12] Thus, it is reasonable to expect that P$\cdot$ add to the double bond of MSD (eq 6), and then the adduct radicals undergo fragmentation to give the polymers (1) with a double bond and cumyl radicals (eq 7). We investigated the volatile products produced after the crosslinking of LDPE in the presence of MSD. From GLC and GC-MS analyses, the formation of a significant amount of biscumyl was confirmed (8.3 mol% based on MSD consumed). This clearly demonstrates that free cumyl radicals are produced in the crosslinking reaction. It is noted that any crosslinked polymers are not produced by the addition-fragmentation reaction. This shows that scorch can be effectively suppressed by the sequential addition-fragmentation reaction of eq 6 and 7.

$$P\cdot \ + \ \underset{\underset{Ph}{|}}{CH_2}{=}\underset{}{C}{-}CH_2{-}\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \ \longrightarrow$$

$$P{-}CH_2{-}\overset{\bullet}{\underset{\underset{Ph}{|}}{C}}{-}CH_2{-}\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \quad (6)$$

$$P{-}CH_2{-}\overset{\bullet}{\underset{\underset{Ph}{|}}{C}}{-}CH_2{-}\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \ \longrightarrow$$

$$P{-}CH_2{-}\underset{\underset{Ph}{|}}{C}{=}CH_2 \ + \ \bullet\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \quad (7)$$

(1)

If the addition-fragmentation reaction occurs until DCP decomposes completely, the formation of crosslinked polymers will be markedly suppressed, resulting in a decrese of crosslinking efficiency by the addition of MSD. However, the maximum torque value was

$$\curlywedge\hspace{-4pt}\curlywedge\bullet \ + \ \underset{\underset{Ph}{|}}{CH_2}{=}\underset{}{C}{-}CH_2{-}\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \ \longrightarrow$$

(MSD)

$$\curlywedge\hspace{-4pt}\curlywedge CH_2{-}\overset{\bullet}{\underset{\underset{Ph}{|}}{C}}{-}CH_2{-}\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \quad (4)$$

$$\curlywedge\hspace{-4pt}\curlywedge CH_2{-}\overset{\bullet}{\underset{\underset{Ph}{|}}{C}}{-}CH_2{-}\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \ \longrightarrow$$

$$\curlywedge\hspace{-4pt}\curlywedge CH_2{-}\underset{\underset{Ph}{|}}{C}{=}CH_2 \ + \ \bullet\underset{\underset{Ph}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \quad (5)$$

increased by the addition of a small amount of MSD. In particular, when 2.5 phr of DCP was used, the addition of 1.0 phr of MSD greatly increased the maximum torque value. This suggests that other reactions leading to the production of highly crosslinked polymers take place after most of MSD was consumed by the above addition-fragmentation reaction. It is conceivable that the polymers (1) further react with polymer radicals to give adduct radicals (2) (eq 8) since 1 has the same reactive double bond activated by the phenyl group as MSD. It would be difficult that the adduct radical (2) undergoes β-scission because of the absence of a good leaving group such as the cumyl group. Even though fragmentation of 2 occurs, it results in only an exchange between PE radicals. Therefore, it is predictable that 2 is stable enough to react with another polymer radical or adduct radical. For example, the reaction of 2 with polymer radicals will lead to the production of the crosslinked polymers having three PE chains *via* combination (eq 9a) or two PE chains *via* disproportionation (eq 9b). Thus, crosslinked polymers will be efficiently produced by these reactions. The detailed mechanistic study on the formation of highly crosslinked polymers are currently underway.
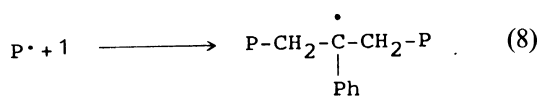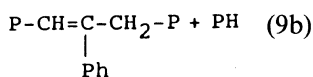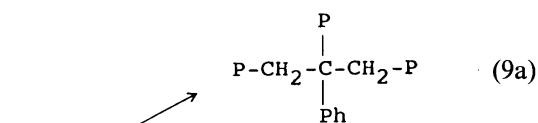
In summary, it was found that MSD acts as both a scorch inhibitor and a crosslinking activator for PE crosslinking. It is suggested that the crosslinking reactions proceed in two stages. In the first stage, addition-fragmentation reaction occurs between MSD and polymer radicals to produce non-crosslinked but reactive polymers with a double bond (inhibition of scorch). And then, polymer radicals efficiently add to the reactive polymers, resulting in the formation of crosslinked polymers (activation of crosslinking).

REFERENCES

1. A. E. Robinson, J. V. Marra, and L. O. Amberg, *Ind. Eng. Chem. Prod. Res. Dev.*, **1**, 78 (1962).
2. L. P. Lenas, *Ind. Eng. Chem. Prod. Res. Dev.*, **2**, 202 (1963).
3. P. O. Tawney, W. J. Wenisch, S. Van Der Burg, and D. I. Relyea, *J. Appl. Polym. Sci.*, **8**, 2281 (1964).
4. R. E. Drake, *Elastomerics*, **114**, 28 (1982).
5. W. C. Endstra, *Kautsch. Gummi Kunstst.*, **43**, 790 (1990).
6. H. K. Latourette and E. R. Gilmont, U.S. Patent 3 202 648 (Aug. 24, 1965).
7. H. R. Larsen, U.S. Patent 3 335 124 (Aug. 8, 1967).
8. J. Groepper, *Gummi Fasern Kunstst.*, **47**, 83 (1994).
9. Y. Watanabe, H. Ishigaki, H. Okada, and S. Suyama, *Chem. Lett.*, 1089 (1993).
10. R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 4395 (1970).
11. J. P. Fischer and W. Luders, *Makromol. Chem.*, **155**, 239 (1972).
12. A. Citterio, A. Arnoldi, and F. Minisci, *J. Org. Chem.*, **44**, 2674 (1979).

$$P\cdot + 1 \longrightarrow P-CH_2-\overset{\displaystyle\cdot}{\underset{\displaystyle Ph}{C}}-CH_2-P \qquad (8)$$

$$(2)$$

$$2 + P\cdot \nearrow \quad P-CH_2-\overset{\displaystyle P}{\underset{\displaystyle Ph}{C}}-CH_2-P \qquad (9a)$$

$$\searrow \quad P-CH=\underset{\displaystyle Ph}{C}-CH_2-P + PH \qquad (9b)$$