

Mechanism for the Peroxide-Initiated Crosslinking of Polyethylene in the Presence of 2,4-Diphenyl-4-methyl-1-pentene

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ABSTRACT: The model reaction for the crosslinking of polyethylene (PE) in the presence of 2,4-diphenyl-4-methyl-1-pentene (α -methylstyrene dimer: MSD) was carried out using *n*-undecane instead of PE and using di-*t*-butyl peroxide as an initiator at 140°C. Undecyl radicals produced by hydrogen abstraction by peroxide radicals from *n*-undecane effectively added to the double bond of MSD to form adduct radicals, which then underwent fragmentation to give olefins and cumyl radicals. The concentration of olefins initially increased, but decreased through a maximum. It was found that the olefins are intermediate products which further react with undecyl radicals, resulting in the formation of compounds with two or three undecyl groups.

KEY WORDS Crosslinking / Polyethylene / Mechanism / Coagent /
 α -Methylstyrene Dimer /

The crosslinking of polyethylene (PE) is conveniently achieved by the use of organic peroxides as crosslinking agents. 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*-phenylene bismaleimide, 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 hydroquinones⁸ act as effective scorch inhibitors for PE crosslinking.

Recently, we reported that 2,4-diphenyl-4-methyl-1-pentene (α -methylstyrene dimer: MSD) is quite a useful coagent for PE

crosslinking.⁹ That is, MSD prevented scorch and also increased the crosslinking efficiency. This result is quite strange since prevention of scorch generally causes a decrease of the crosslinking efficiency if the action mechanism of MSD remains unchanged during the crosslinking. Thus, it was suggested that the action mechanism of MSD would change as the crosslinking reaction proceeds.

To elucidate the crosslinking mechanism of PE in the presence of MSD, we carried out a model reaction using a simple alkane, *n*-undecane, instead of PE. In this paper, we report the results of the detailed products analysis for the model reaction and present a reasonable crosslinking mechanism.

EXPERIMENTAL

Measurements

GLC analysis was performed with a Shimadzu GC-9A gas chromatograph with a flame

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ionization detector using a 15 m fused silica capillary column (0.53 mm in diameter) coated with silicone OV-1. A Shimadzu Chromatopac C-R6A integrator was used for quantitative analysis. Mass spectra were obtained on a JEOL JMS-DX300 mass spectrometer under electron impact conditions.

Materials

2,4-Diphenyl-4-methyl-1-pentene (MSD) and di-*t*-butyl peroxide (DTBP) were received commercially (NOF Corporation). The purities of MSD and DTBP were 95% and 99%, respectively. 2,4-diphenyl-4-methyl-2-pentene (4%) and 1,1,3-trimethyl-3-phenylindane (1%) were included in MSD as isomers. These isomers were inactive under the present reaction conditions.

Reaction Procedure

Typically, a 2 ml of *n*-undecane solution containing 0.2 M of DTBP and 0.1 M of MSD was placed in a glass ampoule. The ampoule was purged with nitrogen, sealed, and immersed in a constant temperature bath regulated at 140°C. After the reaction for a given time, the reaction products were analyzed by GLC and GC-MS in comparison with authentic samples.

RESULTS AND DISCUSSION

Initial Reaction

We carried out a free-radical reaction initiated by DTBP in *n*-undecane in the presence of MSD at 140°C under nitrogen. The reaction products after one hour were analyzed by GLC and GC-MS using authentic samples (Table I). The conversions of DTBP and MSD were 19% and 50%, respectively. Here, the conversion of MSD denotes the conversion of 2,4-diphenyl-4-methyl-1-pentene which is a major component (95%) of MSD. Biscumyl, cumene, α -methylstyrene, and the coupling products of undecyl radicals and cumyl radicals (2) were confirmed as products having the

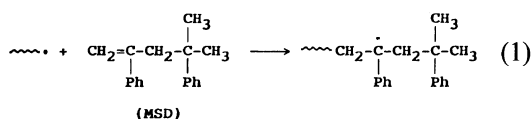
Table I. Products of free-radical reaction initiated by DTBP in *n*-undecane in the presence of MSD at 140°C^a

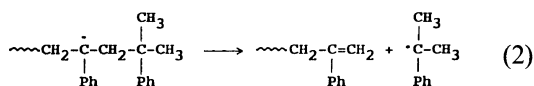
Product	Yield ^b /%
(A) Products with the cumyl fragment	
[PhC(CH ₃) ₂] ₂	74 ^c
PhCH(CH ₃) ₂	11
PhC(CH ₃)=CH ₂	11
PhC(CH ₃) ₂ -R (2)	5
(B) Products with the 2-phenylallyl fragment	
CH ₂ =C(Ph)-CH ₂ -R ^d (1)	94

^a DTBP concn, 0.2 M; MSD concn, 0.1 M; Reaction time, 1 h; DTBP conversion, 19%; MSD conversion, 50%. ^b Mol% yield based on MSD reacted. ^c Yield of cumyl group. ^d R denotes undecyl groups.

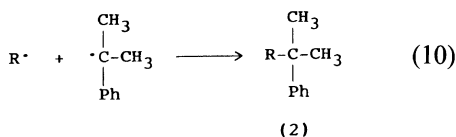
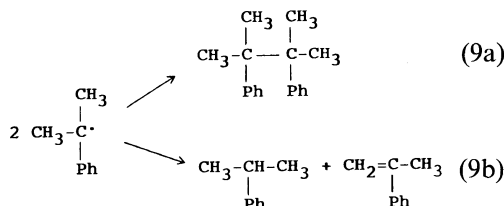
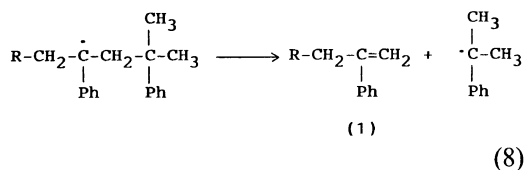
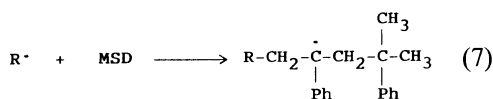
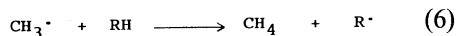
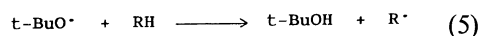
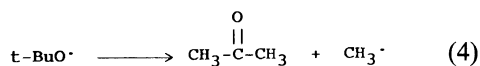
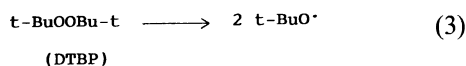
cumyl fragment of MSD. Olefins (1) with undecyl groups were also confirmed as products having the 2-phenylallyl fragment of MSD. The mass spectra of 1 showed the parent peak (M⁺) of 272. The recovery of the cumyl and 2-phenylallyl fragment was pretty high (>90%). These results clearly demonstrate that C-C bond fragmentation between the cumyl group and the 2-phenylallyl group is induced by the attack of undecyl radicals onto MSD.

Recently, we reported that MSD undergoes chain transfer through a free radical addition-fragmentation reaction in styrene polymerization.¹⁰ That is, propagating polymer radicals add to the double bond of MSD to give intermediate adduct radicals (eq 1), and then the adduct radicals undergo fragmentation to expel cumyl radicals (eq 2). The driving force of the addition-fragmentation reaction was rationalized in terms of the activation towards radical addition of the double bond by phenyl group and the presence of the weak C-C bond in a β -position to the adduct radical that can undergo fragmentation.





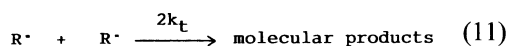
Thus, the reaction products listed in Table I are reasonably explained by the following equations, including the addition-fragmentation reaction between MSD and undecyl radicals.



Here, RH and R \cdot denote *n*-undecane and undecyl radicals with various isomers, respectively. The O–O bond homolysis of DTBP gives

t-BuO \cdot (eq 3), some of which then undergo fragmentation to produce CH $_3\cdot$ and acetone (eq 4). Hydrogen abstraction by *t*-BuO \cdot and CH $_3\cdot$ from RH produces R \cdot (eq 5 and 6). The addition of R \cdot to MSD gives intermediate adduct radicals (eq 7), which then undergo fragmentation to produce olefins (**1**) and cumyl radicals (eq 8). The expelled cumyl radicals mainly undergoes self-combination to give biscumyl (eq 9a). Alternative disproportionation of cumyl radicals gives cumene and α -methylstyrene (eq 9b). The coupling of the cumyl radical and R \cdot produces **2** (eq 10).

In the absence of MSD, the major products were the dehydrodimers of RH, *i.e.*, R–R (0.032 M), which correspond to crosslinked products. However, we could not detect any R–R in the presence of MSD (<0.0005 M). This clearly demonstrates that the addition of R \cdot to MSD (eq 7) is much faster than the bimolecular self-reactions of R \cdot (combination and disproportionation) (eq 11).



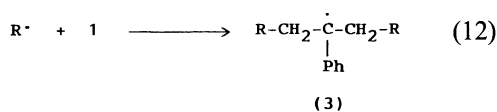
The faster addition reaction seems to be quite reasonable from the following kinetic analysis. The rate for the bimolecular self-reactions of R \cdot (r_1) is expressed as $2k_t[\text{R}\cdot]^2$. It is known that the rate constants of $2k_t$ for simple alkyl radicals are approximately $2 \times 10^9 \text{M}^{-1} \text{s}^{-1}$.¹¹ The concentration of R \cdot depends on the decomposition rate of DTBP. It was reported that the decomposition rate constant of DTBP (k_d) is $6.40 \times 10^{-5} \text{s}^{-1}$ in decane at 140°C.¹² Using the k_d value and applying the steady state assumption to R \cdot , the concentration of R \cdot under the present reaction conditions is estimated as about $1.1 \times 10^{-7} \text{M}$ when DTBP concentration is 0.2 M. Thus, r_1 is estimated as about $2.4 \times 10^{-5} \text{Ms}^{-1}$. On the other hand, the rate for the addition of R \cdot to MSD (r_a) is expressed as $k_a[\text{R}\cdot][\text{MSD}]$, where k_a denotes the addition rate constant. Although the value of k_a is not known, it is assumed to be about the same as that for the rate constant for

addition of 5-hexenyl radical to styrene (k_a') reported by Citterio *et al.*¹³ They presented Arrhenius parameters of $E_a = 4.88 \text{ kcal mol}^{-1}$ and $\log(A/(\text{M}^{-1} \text{ s}^{-1})) = 8.33$ for the addition reaction. Using these parameters, k_a' at 140°C is calculated to be $5.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Thus, the value of r_a is estimated as $6.1 \times 10^{-3} \text{ Ms}^{-1}$ when MSD concentration is 0.1 M . From the comparison between r_i and r_a , we can roughly estimate the rate for addition of R^\cdot to MSD to be about 250 times that for the bimolecular self-reactions of R^\cdot . This kinetic analysis is consistent with the experimental result that R^\cdot predominantly added to MSD.

For the crosslinking of PE, R^\cdot can be considered to be PE radical (P^\cdot). The present products analysis in the initial stage clearly indicates that the formation of P-P would be greatly suppressed by MSD when PE crosslinking is carried out in the presence of MSD. This is consistent with the previous result that scorch is effectively prevented by the presence of MSD for the crosslinking of PE.⁹

Crosslinking Mechanism

The concentration changes of MSD and olefins (**1**) are shown in Figure 1. Interestingly, the concentration of **1** sharply increased at first, but reached a maximum at around 2 h, and then decreased. This clearly demonstrates that **1** is a reactive intermediate. Since **1** has the double bond activated by the phenyl group as well as MSD, it is easily predictable that R^\cdot add to the double bond of **1** to give adduct radicals (**3**) (eq 12).



With decreasing **1**, several peaks appeared in the region of longer retention times than **1** on the GLC chart. These peaks were divided into two groups which greatly differ from one another in retention times. The mass spectra of the former group showed the parent peak (M^+) of 426 or 428, and those of the latter

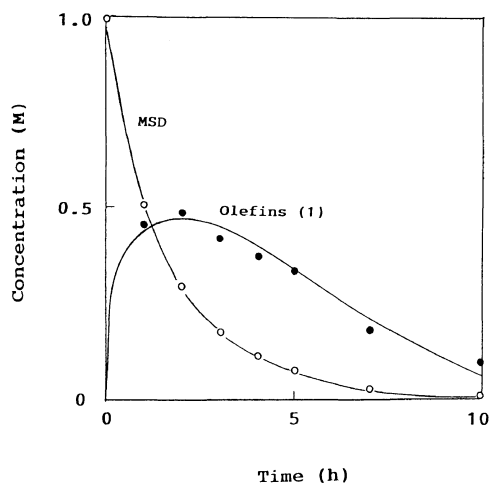
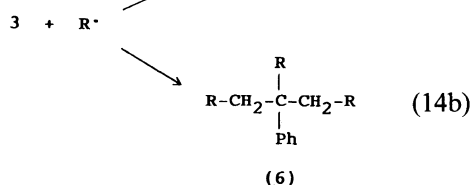
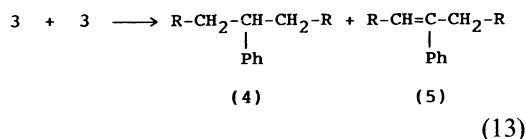


Figure 1. Concentration changes of MSD and **1** during the free-radical reaction initiated by DTBP in *n*-undecane in the presence of MSD at 140°C : (○), MSD; (●), **1**; DTBP, 0.2 M .

showed M^+ of 582. From these parent peaks and fragment peaks, it was found that the former group consists of the compounds (**4**) and (**5**) with two R groups and the latter consists of the compound (**6**) with three R groups. The formation of these compounds with two or three R groups is explained by the following equations.



The disproportionation reaction of **3** results in the formation of **4** and **5** (eq 13). Also, the disproportionation reaction of **3** and R^\cdot leads to the formation of **5** (eq 14a). The combination reaction of **3** and R^\cdot leads to the formation of

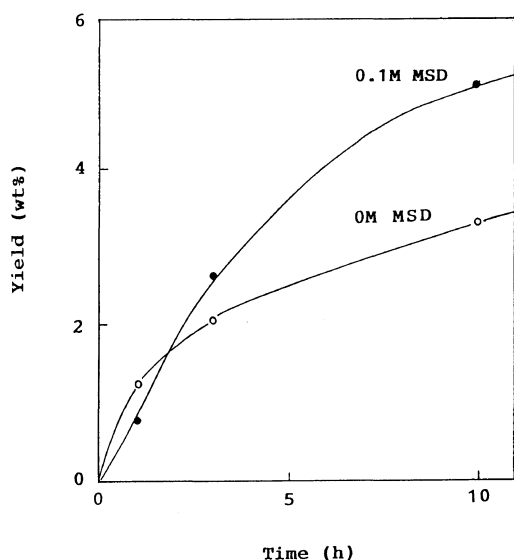


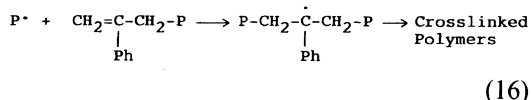
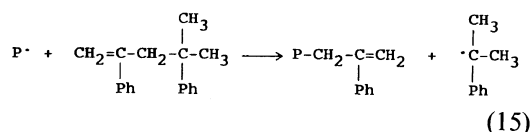
Figure 2. Yields of compounds with two or three R groups produced in free-radical reaction initiated by DTBP in *n*-undecane at 140°C: (○), 0 M MSD; (●), 0.1 M MSD; DTBP, 0.2 M.

6 (eq 14b).

Each yield of **4**, **5**, and **6** could not be determined by GLC due to their broad peaks. So, after the reaction for given times, we removed the low boiling materials by evaporation and measured the total weight of compounds **4**, **5**, and **6**. Similarly, in the absence of MSD, the yield of R–R was determined. The results are shown in Figure 2. Evidently, in the initial stage, the yield of compounds with two or three R groups in the presence of MSD was lower than that in the absence of MSD, but in the later stage the situation became reversed. This result is consistent with the previous result obtained in the crosslinking of PE in the presence of MSD.⁹ That is, when MSD was added, torque increased more mildly at 140°C (initial stage), but increased more rapidly and reached a higher maximum value at 180°C.

Thus, the production of highly cross-linked polymers in PE crosslinking in the presence of MSD is ascribed to the formation of the reactive olefinic intermediates which can further react with polymer radicals.

In conclusion, the crosslinking of PE in the presence of MSD proceeds in two stages. In the first stage, addition-fragmentation reaction occurs between MSD and polymer radicals to produce reactive olefins (eq 15). And then, the olefins react with polymer radicals to produce crosslinked polymers (eq 16).



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