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Addition-Fragmentation Chain Transfer in Free Radical Styrene Polymerization in the Presence of 2,4-Diphenyl-4-methyl-1-pentene

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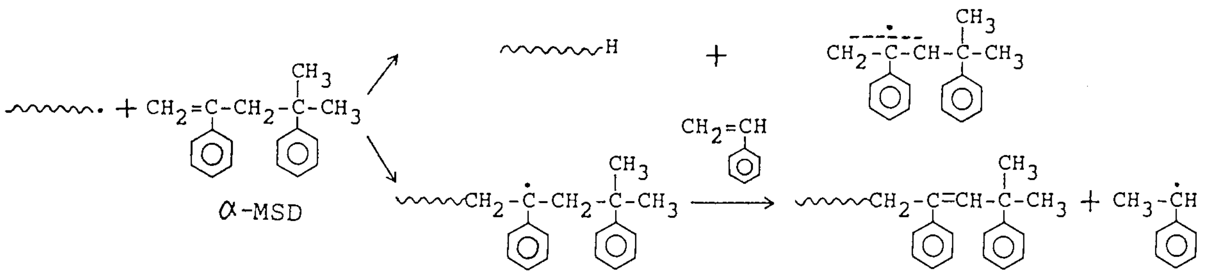
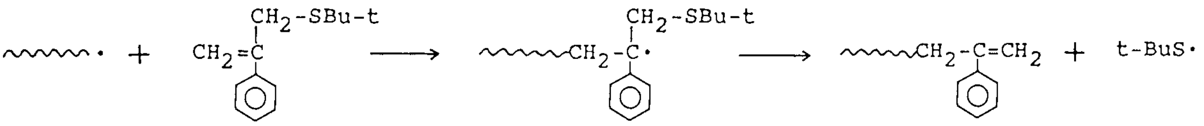
Thermal polymerization of styrene in the presence of 2,4-diphenyl-4-methyl-1-pentene (α-MSD) gave a low molecular weight polymer having a terminal double bond and a cumyl moiety without lowering the polymerization rate. A chain transfer mechanism through addition-fragmentation reaction is presented.

In free radical polymerization, polymer molecular weight can be controlled with appropriate chain transfer agents such as carbon tetrachloride and mercaptanes. 2,4-Diphenyl-4-methyl-1-pentene, i.e., α-methylstyrene dimer (α-MSD), is also known to be an effective chain transfer agent for styrene polymerization.[1,2] Fischer and Lüders[1] proposed that the chain transfer would proceed through allylic hydrogen abstraction by polymer radical (Eq. 1a) and/or addition of polymer radical to α-MSD and subsequent hydrogen atom transfer to styrene (Eq. 1b). However, the detailed mechanistic studies have not been made so far.



(1a)
(1b)

Recently Meijs et al.[3,4] have reported that allylic compounds activated by phenyl, alkoxy carbonyl, and cyano groups undergo chain transfer via sequential radical addition and fragmentation reactions (Eq. 2).


(2)

Since α-MSD is one of activated allylic compounds, it is expected that the similar addition-fragmentation reaction may occur in free radical polymerization in the presence of α-MSD. In this paper, we present a clear chain transfer mechanism of α-MSD in styrene polymerization.

The thermal polymerization of styrene was carried out in the presence of α-MSD in benzene at 140 °C. The results are shown in Table 1. The polymers prepared in the presence of α-MSD were of markedly lower molecular weight compared with that prepared in the absence of α-MSD. For example, the presence of ca. 5 vol% of α-MSD in styrene-benzene (1:1 vol) lowered the molecular weight by a factor of 20. However, α-MSD had no effect on the polymerization rate. These results indicate that α-MSD acts as a true chain transfer agent without retarding styrene polymerization.

To clarify the chain transfer mechanism, low molecular weight polystyrene samples were prepared in the presence of α-MSD. After purification by repeated precipitation to remove a trace of unreacted α-MSD, the samples were examined by ^{1}H NMR spectroscopy (270 MHz). The ^{1}H NMR spectra of the samples of $\overline{M}_n$=4300 and 3000 are shown in Figs. 1 and 2. Besides the signals due to styrene unit (i.e., 1.7, 2.2, and 6.4-7.2 ppm), low intensity signals around 1.0 ppm, and centered at 4.8 and 5.1 ppm were observed with each sample. The latter two signals of equal intensities around 5 ppm are characteristic of the resonances of the two protons of the terminal double bond. Furthermore, Meijs et al.[3)] reported that a low molecular weight polystyrene ($\overline{M}_n$=3600) prepared with allylic sulfide as a chain transfer agent exhibited ^{1}H NMR signals at 4.7 and 5.0 ppm which were ascribed to the terminal double bond of the polystyrene. Thus, it may be concluded that the chain transfer reaction of α-MSD with polymer radical give a polystyrene having a terminal carbon-carbon double bond.

Table 1. Thermal polymerization of styrene in the presence of α-MSD in benzene at 140°C

α-MSD[a)] %	Time h	Conversion %	$10^{-3}\overline{M}_n$[b)]	$\overline{M}_w/\overline{M}_n$[b)]
0	10	65.7	116	1.71
0	20	78.8	105	1.77
4.8	10	63.6	6.7	2.27
4.8	20	74.8	5.9	2.42
9.1	10	63.5	3.0	2.10
9.1	20	73.1	2.9	2.17

a) Vol % of α-MSD in styrene-benzene=1:1 (vol).

b) Determined by gel permeation chromatography (GPC).

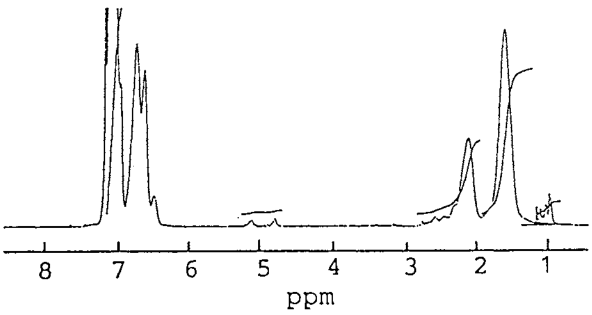


Fig. 1. 270 MHz ^{1}H NMR spectrum of the purified polystyrene ($\overline{M}_n$=4300) prepared with α-MSD.

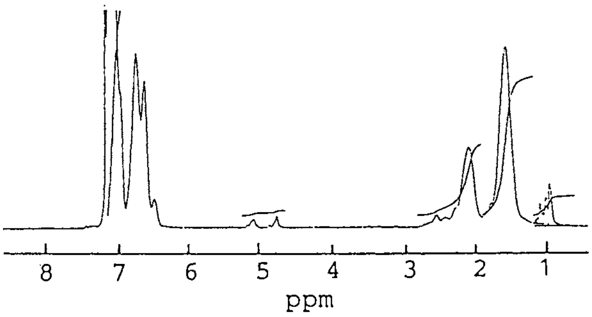


Fig. 2. 270 MHz ^{1}H NMR spectrum of the purified polystyrene ($\overline{M}_n$=3000) prepared with α-MSD.

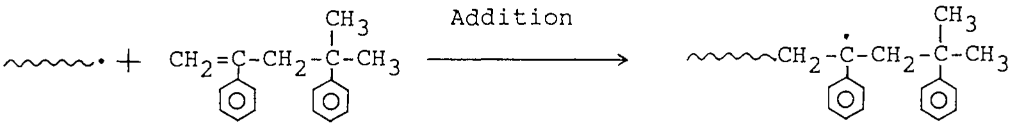
Using GPC-derived molecular weight ($\overline{M}_n$) and the intensity ratio of signals due to the terminal double bond and the methine of polystyrene main chain (2.2 ppm), the average numbers of the terminal double bond per polymer chain for the polystyrenes of $\overline{M}_n$=4300 and 3000 were calculated to be 0.96 and 0.93, respectively (Table 2).

If the chain transfer reaction occurs according to Eq. 1b as proposed by Fischer and Lüders, the resulting polymer must include the internal double bond. Likewise, if Eq. 1a is a major chain transfer reaction and the allyl radical so formed reinitiates the polymerization of styrene, mixed polymers with the terminal and internal double bond will be produced. However, as shown in Figs. 1 and 2, the characteristic signal demonstrating the presence of the internal double (around 6 ppm) could not be observed. To explain the quantitative formation of the terminal double bond, we propose a chain transfer mechanism through addition-fragmentation reaction. That is, polymer radical adds to the terminal double bond of α-MSD (Eq. 3), and then the adduct radical undergoes fragmentation to give a cumyl radical and a polymer with a terminal double bond (Eq. 4). Possibly, the latter reaction is a facile process since cumyl radical (tertiary radical) is more stable than polymer radical (secondary radical).

Table 2. Characteristics of polystyrenes prepared with α-MSD$^{a)}$

α-MSD$^{b)}$	Time	Conversion	$\overline{M}_n$$^{c)}$	Average No. per polymer chain$^{d)}$	
%	h	%		Terminal C=C	Cumyl moiety
4.8	40	66	4300	0.96	1.1
9.1	40	66	3000	0.93	1.2

a) Thermal polymerization in benzene at 140°C. b) Vol % of α-MSD in styrene-benzene=1:3 (vol). c) Determined by GPC. d) Calculated from $\overline{M}_n$ and ^{1}H-NMR data.



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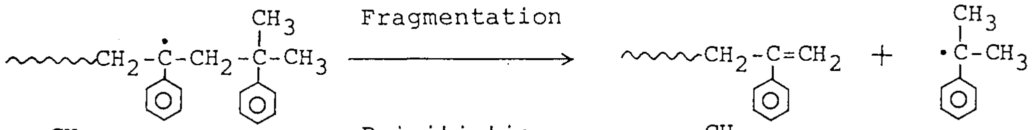

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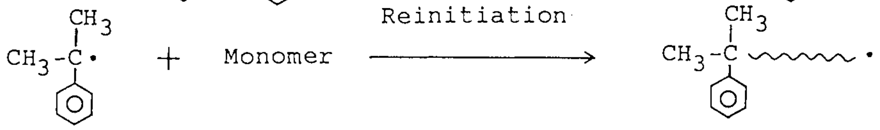
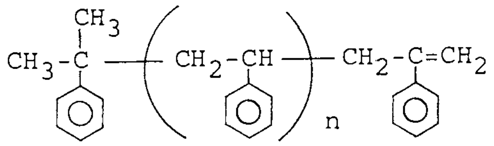


(5)

In view of the fact that α-MSD undergoes true chain transfer (Table 1), the expelled cumyl radical will reinitiate styrene polymerization effectively (Eq. 5). The ^{1}H NMR signals around 1.0 ppm clearly demonstrates that the cumyl fragment is incorporated into polymer chain. From the calculation of the average number of cumyl moiety per polymer chain, it was found that about one cumyl moiety is attached to polymer chain (Table 2). Thus, most of the polystyrenes prepared with α-MSD can be expressed as the following structure in which polymer main chain is inserted into the weakest C-C bond of α-MSD.



In conclusion, it has been shown that α-MSD is a typical addition-fragmentation type of chain transfer agent for free-radical styrene polymerization. Although a number of addition-fragmentation reactions involving C-S, C-Br, or C-O bond cleavage have been reported,$^{3-5)}$ the present study is the first to have clearly demonstrated that C-C bond cleavage occurs by addition-fragmgentation reaction.

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