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Mechanistic consideration for the thermal degradation of polymers based on continuous flow operation

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Abstract

In this study, the author investigated the validity of the radical transfer mechanism for thermal degradation of polymers based on experimental facts and macroscopic considerations. There are various insufficiencies in the radical transfer mechanism which cannot provide any mechanistic explanation, such as the existence of gas-liquid interface in the chemical reaction dominant field, the effect of pressure on the thermal degradation behavior of polymers, and the temperature drop from liquid to gas phase in the reactor.

These insufficiencies indicate that the radical transfer mechanism alone cannot explain the entire process of the thermal degradation of polymers. The generation of volatile products requires a different mechanism than the radical transfer. The author proposed a hydrogen transfer mechanism for breaking the chain-end that produces the volatile, and discussed its

consistency with the observed facts.

Keywords: Thermal degradation; Polymer; Radical transfer mechanism; Hydrogen transfer mechanism; Macroscopic mechanism; Insufficiency

1. Introduction

In 1935 Hermann Staudinger, who was awarded the Nobel Prize in Chemistry for his discoveries in the field of macromolecular chemistry, published a paper on the mechanism in the thermal degradation of polymers [1]. In the paper, for polystyrene, Staudinger proposed a hydrogen transfer mechanism to explain scissions of C-C chain bonds. This mechanism involves a hydrogen transfer at the site of a scission to yield one unsaturated and one saturated end. Since then, this mechanism has been extended and modified to explain the experimental results of thermal degradation of polystyrene, polyolefins and related polymers [2,3]. According to this mechanism, most of the C-C chain scissions are caused by strains formed in the polymer chains because of thermal vehement movement.

On the other hand, in the 1950s Simha et al. proposed a radical transfer mechanism to explain the scission of C-C bonds during the thermal degradation of polymers [4-6]. Their radical transfer mechanism consists of several steps, namely, initiation, propagation, free-radical transfer and termination. Thereafter, since this mechanism seems to explain satisfactorily the product distribution in the thermal degradation of polymers, it has come to be accepted that the thermal degradation of polymers proceeds through the radical transfer mechanism and it has been cited in many related papers [7-9]. In particular, their papers were preferentially referred in the mechanics consideration that was put into the research work in which the product derived from the thermal degradation of polymers was analyzed by gas

chromatography with a capillary column [10-13]. But it has been hardly taken notice of the reaction rate, and the reaction system generating the thermal degradation of polymers.

In recent years, Faravelli et al. [14-18] and Broadbelt et al. [19-25] have done extensive works for the kinetic modeling of the thermal degradation of vinyl polymers conforming basically with the radical transfer mechanism. However, they have not aimed at the proof itself of the mechanism and have not taken notice of the feature of the reaction system generating the thermal degradation of polymers, that is, the rate controlling step, the gas-liquid interface in working reactor, the temperature drop from liquid to gas phase, the effect of pressure on the rate, the product distribution and so on. Even though they definitely contributed to the modeling of the thermal degradation of polymers on the basis of the radical transfer mechanism.

Now then, what's come out on the mechanism of the thermal degradation of polymers in a time between Staudinger and Simha et al.? Nothing, there does not appear any experimental fact or evidence enough to prove the radical transfer mechanism for the present. At least we are not able to declare that the radical transfer mechanism is a proved mechanism, because it is an assumed reaction scheme, as mentioned by Simha himself in his paper [4]. Moreover, there exist not a few doubts as to the radical transfer mechanism for the thermal degradation of polymers.

For example, S.L.Madorsky mentioned the radical transfer mechanism [26], as follows, "According to this mechanism, the free-radical transfer reaction takes place in two separate steps, one in which the free radical is formed, and the other in which it abstracts a hydrogen from its own or another chain. The question arises why unzipping of the free radical does not take place during the interval between these two steps and thus yield a larger amount of monomer than is actually the case".

Similarly, there are various inconsistencies between the usual radical transfer mechanism and

the observed fact in the thermal degradation of polymers. They show that the radical transfer mechanism alone cannot explain the entire process of thermal degradation of polymers. The generation of volatile substances requires a different mechanism than the radical transfer. In the present paper the author pointed out some insufficiencies and inconsistencies in the radical transfer mechanism for the thermal degradation of polymers based on the experimental fact observed by continuous flow operation and the macroscopic consideration. Then the author proposed the chain-end scission accompanying a hydrogen transfer to generate volatile products and discussed its consistency with observed facts.

2. Insufficiencies in the conventional radical transfer mechanism

2.1 Gas-liquid interface in working reactor and the rate controlling step

The activation energy of a physical process does not exceed 10kcal/mol. Generally speaking, when a physicochemical process has an activation energy of less than 10kcal/mol, a physical process such as vaporization takes the role of rate controlling step. On the contrary, when the activation energy is greater than 30kcal/mol, we conclude that a chemical reaction plays the role of rate controlling step in that process [27].

All of the activation energies calculated from the rate analysis of the thermal degradation of polymers in the literature are higher than 30kcal/mol [26, 28-34]. That is, the thermal degradation of polymers is a rate process in which a chemical reaction plays the role of rate controlling step.

On the other hand, most of researchers have not referred to the physicochemical significance that there exists a gas-liquid interface to separate the gas (volatile product) and the liquid (reactor content) in the working reactor generating the volatile. One of the reason would be that most of the previous works on the thermal degradation of polymers were carried out by

using a batch reactor system with a small amount of sample.

Anyway, the thermal degradation of polymers is a rate process in which a chemical reaction plays a role of the rate controlling step, and besides there exists a gas–liquid interface which separates the reactant (reactor content) and the product (volatile product) in the working reactor. In addition, as shown in Fig. 1, all products pass through the gas-liquid interface in the working reactor and exit the reactor. It exactly indicates that the vaporization of the product into gas phase always have the same rate as the formation of the product in liquid phase. That is, during the thermal degradation of polymers in this reaction system, the vaporization has the activation energy that is equivalent to the one of a chemical reaction.

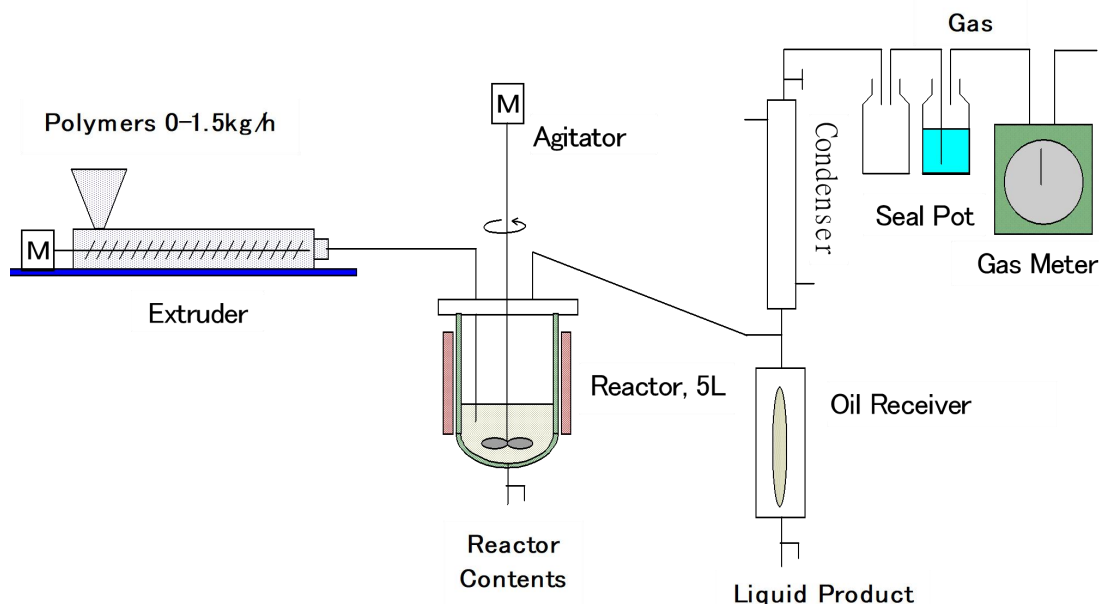


Fig. 1 Continuous flow reactor for thermal degradation of polymers

The above-mentioned consideration leads to an important conclusion that the process of volatilization during the thermal degradation of polymers must be a kind of reaction but not a physical process. Consequently, the generation of the volatile product in the thermal degradation of polymers is a heterogeneous reaction in which the reactant is in a liquid phase and the product is in a gaseous phase [28].

Usually, rates of the thermal degradation of polymers are expressed by various measures, such

as the weight reduction of original sample, the amount of volatile product, the double bond formation in the volatile product and the like. These values are entirely determined based on the phenomenon that comes out through the gas-liquid interface. That is, the reaction rate must be equal to the rate of vaporization, regardless of where the volatile product is formed in the liquid phase and then vaporized into the gas phase to emerge as the volatile product. Therefore, the vaporization process in the thermal degradation of polymers must be a kind of chemical reaction in which the reactant is in the liquid phase and the product is in the gas phase, i.e. a heterogeneous reaction.

When Faravelli et al. applied a rate of the gas phase pyrolysis (homogeneous reaction) in their works for the kinetic modeling of the thermal degradation of vinyl polymers, they corrected it by vaporization [16]. However, there does not exist a process of vaporization in a homogeneous system. It is considered that they already have recognized the existence of a gas-liquid interface in the working reactor generating the volatile.

The gas phase pyrolysis is a reaction differed from the thermal degradation of polymers. The former one is a homogeneous reaction caused in the temperature of over 600°C for a gaseous hydrocarbon, and the latter is a heterogeneous reaction caused in the temperature range of 300-500°C for a macromolecule. And the product distribution quite differs from each other too.

2.2 Temperature drop from liquid to gas phase

There invariably appears a temperature drop of 50-150°C from the liquid to the gas phase in the reaction system generating the thermal degradation of polymers as shown in Fig. 2 [29]. It is impossible for the usual radical transfer mechanism to give a mechanism-based explanation for this temperature difference between the gas and the liquid phase.

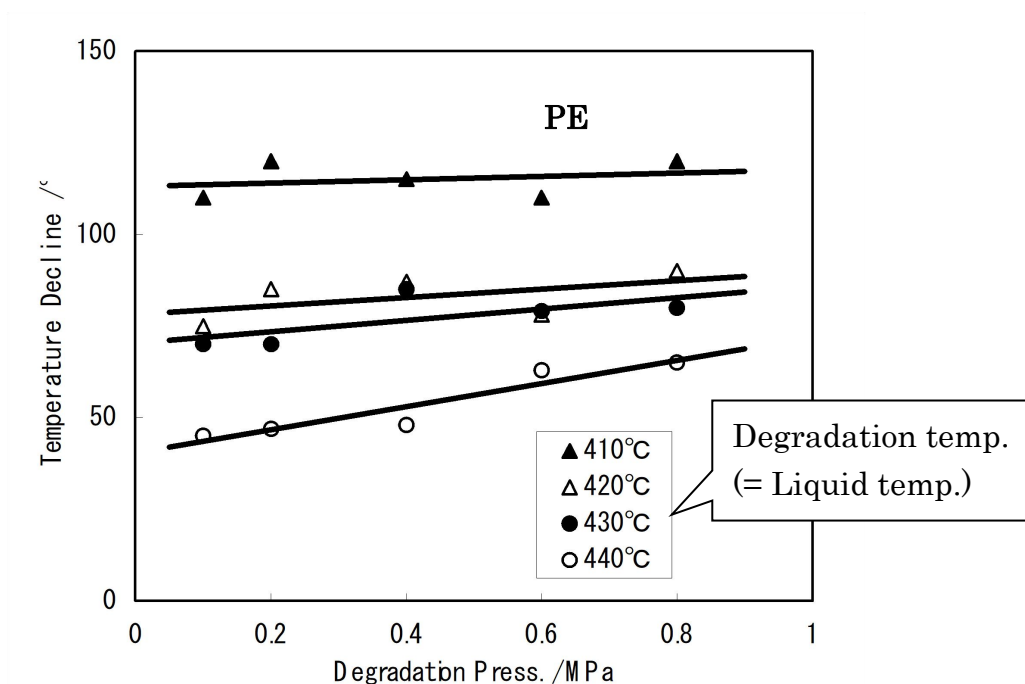


Fig.2 Temperature drop from liquid to gas phase in the continuous flow reactor [29]

When a simple vaporization of a liquid occurs, there will not be an appreciable difference in temperature between the vapor and the liquid phase in vessel. In a process of vaporization, the change of state from liquid to vapor compensates the latent heat of vaporization. But for the thermal degradation of polymers, the change from the liquid (reactor contents) to the gas (volatile products) involves the change of substance as well as the state.

When we attempt to estimate an enthalpy change from state A to B in a system, we can choose any route going from A to B according to Hess's law. In order to estimate the enthalpy change from reactor contents to volatile products in the reaction system generating thermal degradation of polymers, we choose a route along that reactor contents vaporize into gas phase and then decompose to volatile products.

For the resultant change of state from reactor contents to volatile products, the heat of vaporization is compensated by the change of state, but the heat of thermal decomposition must be compensated by the heat capacity of volatile products. Consequently, there must exist

a temperature drop from the liquid phase (reactor contents) to the gas phase (volatile products) to counterbalance the heat of thermal degradation.

Because the enthalpy change from reactor contents to volatile products involves not only the heat of vaporization but also the heat of thermal decomposition, it is not enough for the heat of vaporization to compensate the change of state from liquid to gas. Thus, it brings about a temperature drop in the working reactor generating the volatile.

With the usual radical transfer mechanism, where the formation of volatiles is merely evaporation of the decomposition products, it is not possible to give a mechanism-based explanation for this temperature difference between the gas and the liquid phase.

2.3 Effect of pressure during the thermal degradation of polymers

In the previous papers [29, 35, 36], the author reported that the reaction pressure had a significant effect on the rate and the distribution of degradation products during thermal degradation of polyethylene, polypropylene and polystyrene, respectively. There exists a one to one correspondence between the double bond formation and the scission of C-C links in polymer. When the rate of double bond formation changes with pressure as shown in Fig. 3 [29], we can conclude that the pressure takes part directly in the scission of C-C links during the thermal degradation of polymers. The usual radical transfer mechanism can not give a mechanism-based explanation for the effect of pressure in the thermal degradation of polymers.

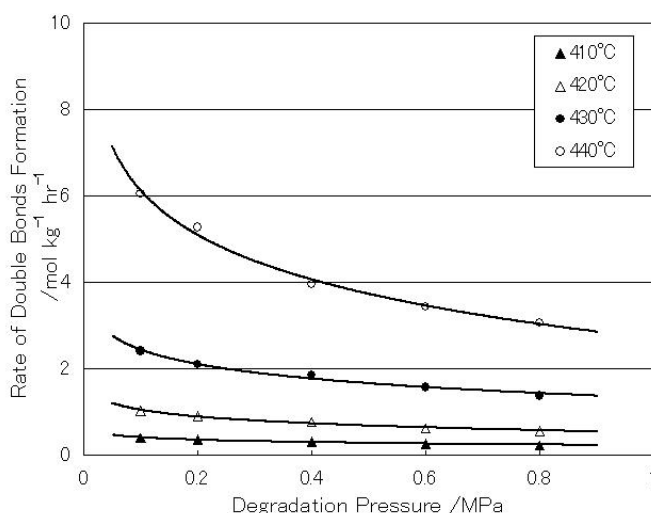


Fig. 3 Effect of pressure on the rate of double bond formation of PE [29]

In the preceding paper [28], the authors proposed a macroscopic mechanism that the thermal degradation of polymers consists of two sorts of scission, which simultaneously occur in the reactor. One is a random scission of C-C links which causes molecular weight reduction of raw polymer increasing the reactor content in liquid phase, and the other is a chain-end scission of C-C links which causes a dissipation of the reactor content generating volatile products. The latter one, the chain-end scission, takes place at gas-liquid interface in the working reactor. It is the chain-end scission that the reaction pressure has an effect on.

With the usual radical transfer mechanism, where the formation of volatiles is merely vaporization of the decomposition products, it is not possible to give a mechanism-based explanation for the pressure effect on the scission rate of C-C links in the thermal degradation of polymers.

2.4 Existence of long chain molecules in volatile product

Recently, it has been found that heavy compounds with boiling points much higher than the pyrolysis temperature are present in the volatile product. Using Q-TOF MS, hydrocarbon chains as long as nC75 (molecular weight of 1052) in the liquid products of polyethylene were identified by Brebu et al. [37], as shown in Fig. 4.

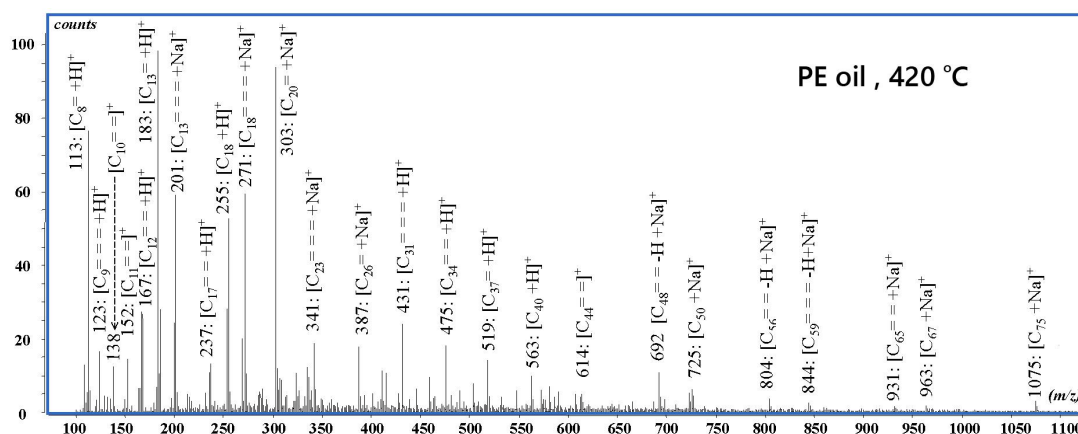


Fig. 4 Q-TOF MS spectra of the oil obtained from PE at 420 °C

They also found compounds with molecular weights as high as 1345 and 946, corresponding to unsaturated aliphatic C96 and styrene nonamar structure, respectively, from the pyrolysis of polypropylene and polystyrene. With the usual radical transfer mechanism, where the formation of volatiles is merely vaporization of the decomposition products, it is not possible to give a mechanism-based explanation for the vaporization of such a long chain molecule. It is the chain-end scission at gas-liquid interface, according to Murata mechanism [29], that can explain the presence of such compounds in pyrolysis oils.

The above insufficiencies cause various inconsistencies in the interpretation of thermal degradation of polymers by the radical transfer mechanism. In the following section a couple of inconsistencies will be shown that occurs if the radical transfer mechanism governs the entire process, including the generation of volatile, in the thermal degradation of polymers.

3. Inconsistency between the radical transfer mechanism and the observed fact

In this section various inconsistencies of the usual radical transfer mechanism are illustrated based on the experimental result observed by the thermal degradation of polystyrene with continuous flow operation. The author has previously reported similar experimental results of

polystyrene (Temperature: 5 levels) [38], but here we will discuss it based on the experimental results carried out again.

3.1 Experimental

Fig. 1 shows a schematic diagram of the experimental set-up used for the thermal degradation of polystyrene (PS) under continuous flow operation. The thermal degradation was performed in a stainless steel vessel reactor of 5 l volume in which a rotating stirrer was installed. The details of materials, the experimental procedure and the analytical methods were described in the preceding paper [28].

In this paper, ‘volatile products’ refers to the gaseous and liquid products, and ‘degradation products’ refers to the volatile product and the reactor content.

3.2 Results and Discussion

3.2.1 Rate of thermal degradation of PS

Fig. 5 shows the rates of PS thermal degradation which were observed by the continuous flow reactor shown in Fig. 1. The definitions of the rates of thermal degradation (the mass rate of volatilization and the rate of double bonds formation) are given by Eq. 1 and 2.

The mass rate of volatilization (h^{-1}) =

$$\text{volatilization rate (kg h}^{-1}\text{) / amount of reactor content (kg)} \quad (1)$$

The rate of double bonds formation ($\text{mol kg}^{-1} \text{h}^{-1}$) =

$$\text{C=C bonds in volatile (mol h}^{-1}\text{) / amount of reactor content (kg)} \quad (2)$$

The amount of C = C bonds in volatile was determined based on the bromine number of the liquid product and the gas chromatography data of the gaseous product. The double bond in degradation product is a direct measure for the breakage of polymer links, because there exists a one to one correspondence between the breakage of C-C links and the formation of double

bonds.

The activation energy of PS thermal degradation was 50kcal/mol, which was calculated from the mass rate of volatilization. As mentioned before, we can conclude that PS thermal degradation in this reactor system is a chemical reaction dominant process.

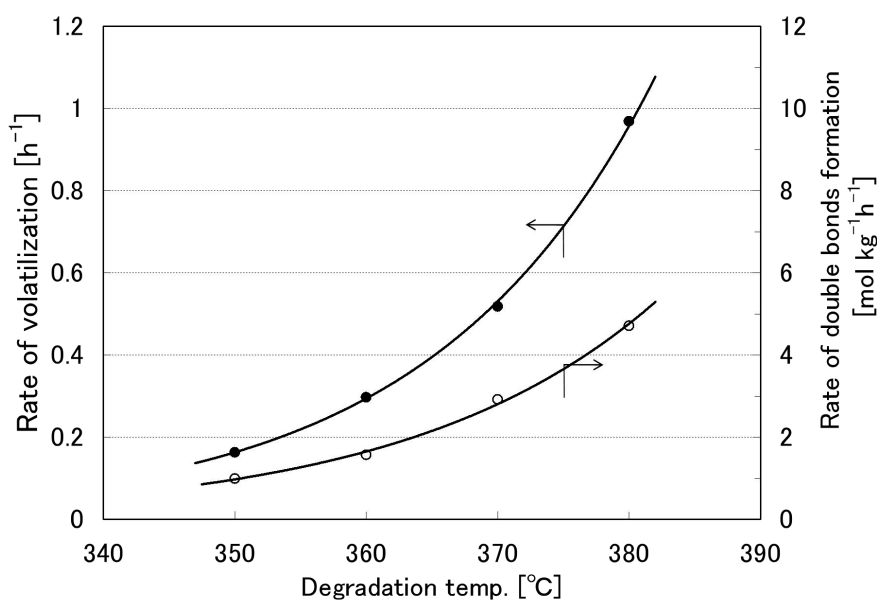


Fig. 5 Rate of thermal degradation of PS observed by the continuous flow reactor shown in Fig.1

In the preceding papers [28, 29], we have explained about DVR (Degradation and Volatilization Reactor), a continuous flow reactor system such as shown in Fig. 1. The DVR is a continuous flow stirred tank reactor in which the thermal degradation of polymers and the generation of volatiles simultaneously occur under a steady state. In DVR, the input polymer is continuously melted into a viscous liquid and mixed with the reactor content. At degradation temperature, the reactor content is a liquid thermally decomposing into small molecules which are convertible to hydrocarbon vapor and leave the reactor. As shown in Fig. 1, all volatile products vaporize in reactor before coming out as the output product of DVR. Thus, there coexist gas (volatile products) and liquid (reactor content) in DVR, that is, there is a gas-liquid interface in the working reactor.

In the present study the author carried out PS thermal degradation in the DVR system to

investigate the temperature effect on the reaction rate and the product distribution under atmospheric pressure. Then the mechanistic consideration for the thermal degradation of polymers was done based on the observed information.

3.2.2 Degradation products

Gaseous product:

The thermal degradation of PS provided a small amount of gaseous products that is less than 0.15wt% of the volatile product. For PS thermal degradation, the gaseous product was mainly hydrogen, since the breakage of C-C main bonds does not bring about any gaseous product. And it is not until 800°C that the breakage of side chain begins and benzene increases in the pyrolysis product [39].

Liquid product:

The liquid product yield of 99.9wt% was obtained for PS thermal degradation in this continuous flow operation. Physicochemical properties of the liquid products resulted from PS were also shown in the preceding paper [28, 38]. Fig. 6 shows a carbon number distribution (NPgram) of the liquid product. The liquid product obtained by PS thermal degradation can be characterized by NPgram (Normal Paraffin gram) demonstrated by Murata and Makino [34]. NPgram is a carbon number distribution of the liquid hydrocarbon which is composed by the gas-chromatogram on the basis of boiling points of a series of normal paraffins. The detail of NPgram is mentioned in the preceding papers [28, 35]. The author has extended the application of NPgram for various hydrocarbon oils, such as waste plastics derived oil, petroleum fractions and coal derived oil [40].

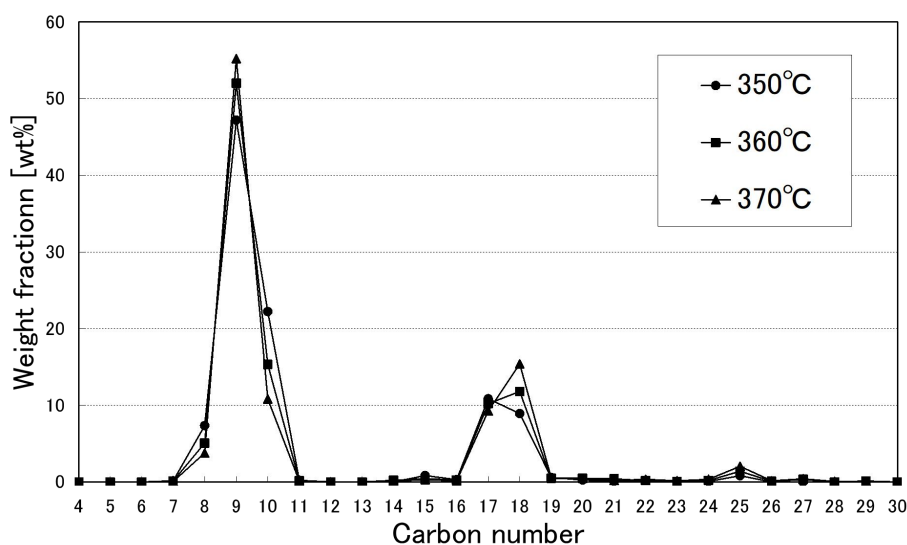


Fig. 6 Carbon number distribution (NPgram) of liquid products derived from PS

Table 1 Constituents derived from thermal degradation of polystyrene and their assignments on NPgram

Carbon number on NPgram	Component
7	Benzene
8	Toluene
9	Ethyl benzene
	Styrene monomer
	Cumene
10	Aryl benzene
	α -Methyl styrene
17	1,3-Diphenyl propane
18	Styrene dimer
25	Styrene trimer

The NPgram of the liquid product derived from PS has peaks at 9, 18 (or 17) and 25. Table 1 reveals major constituents contained in the liquid product of PS and their corresponding carbon numbers in NPgram. Peak components at 9, 18 and 25 in NPgram involve monomeric constituents, such as monomer, dimer and trimer, respectively. Thus, monomeric constituents are major products in PS thermal degradation.

As shown in Fig. 6 and Table 1, the liquid product of PS does not contain a constituent less than carbon number 6 in NPgram. Benzene is assigned to nC7 and toluene to nC8 in NPgram. In this paper, nC6, nC7, nC8, --- refer to the carbon numbers in NPgram. On the other hand, C6, C7, C8 --- refer to the actual carbon numbers of organic compounds.

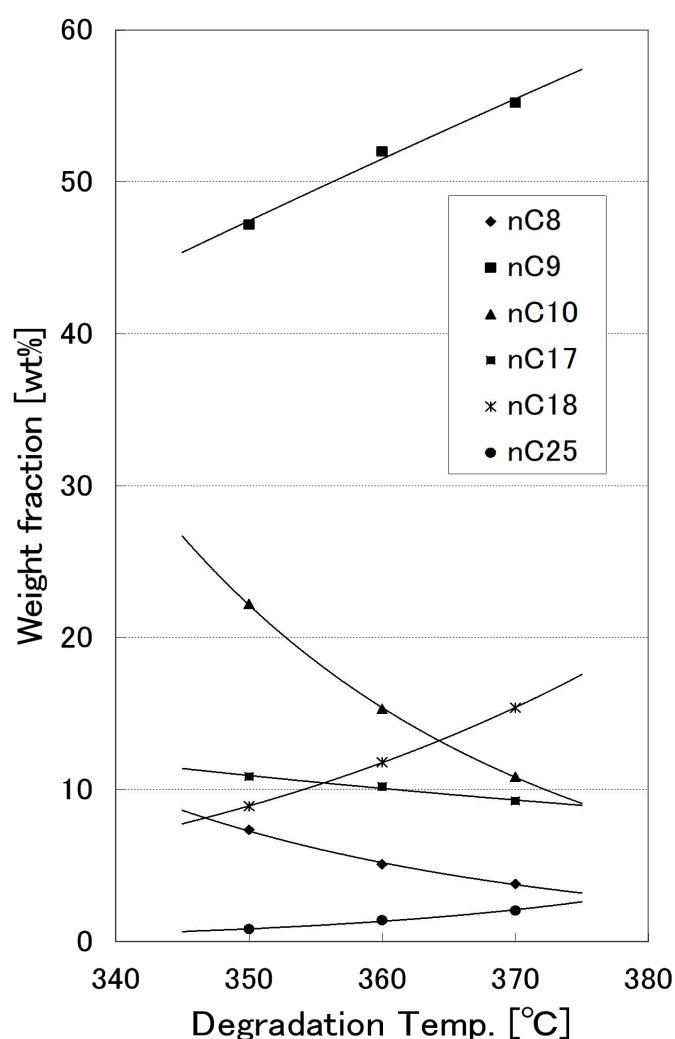


Fig. 7 Temperature dependence of components assigned to individual carbon numbers on NPgram

Ethyl benzene, styrene monomer and cumene belong to nC9 in NPgram, and they account for more than 50 % of the liquid product of PS. Two constituents are assigned to nC10. One is α -methyl styrene that accounts for 99% of the nC10 component, the other is allyl benzene for the rest. 1,3-Diphenyl propane is assigned to nC17, styrene dimer (2,4-Diphenyl-1-butene) to nC18, and styrene trimer to nC25, respectively. Constituents other than the above-mentioned

accounted for 2~3 wt% of the liquid product, even though more than 20 peaks were found on the gas-chromatogram of the liquid product. Fig. 7 shows the temperature tendency of the major components in NPgram. It reveals that there are two distinct groups. The one has a tendency to increase and the other to decrease with the degradation temperature.

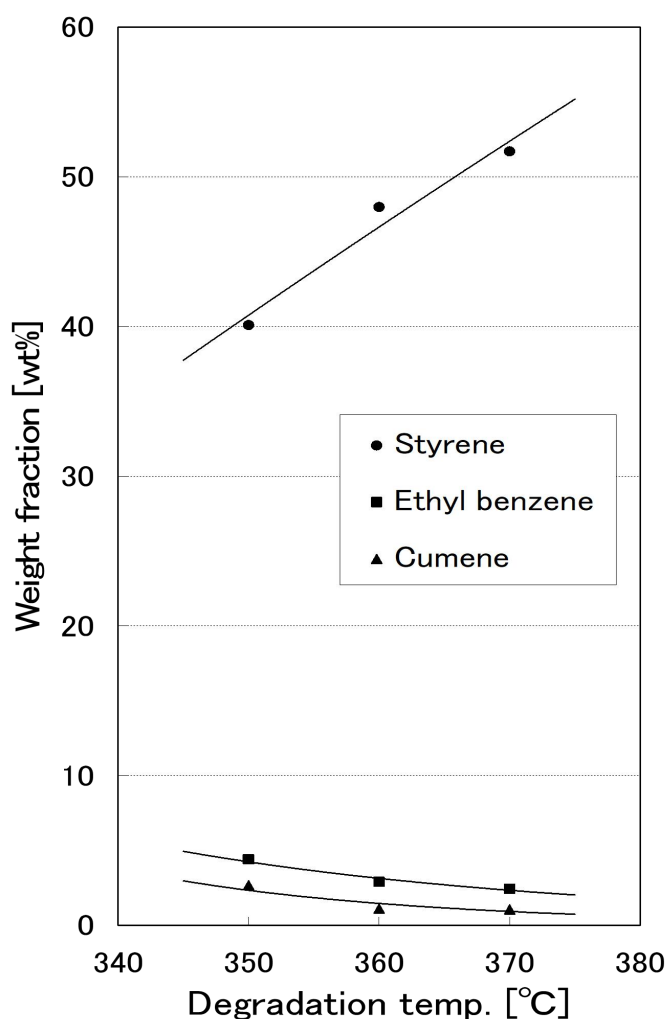


Fig. 8 Components assigned to the carbon number 9 on NPgram

Referring to the assignment shown in Table 1, we can see that the weight fractions of components which contain monomeric constituents, such as monomer, dimer and trimer, increase with degradation temperature. On the contrary, the weight fractions of components that do not contain monomeric constituents decrease with the degradation temperature. For more detail, the weight fractions of constituents assigned to nC9 were separately plotted in

Fig. 8.

It is evident that the increase of nC9 component comes from that of styrene monomer, since the others, ethyl benzene and cumene decrease with temperature. Similarly, the increase with temperature of nC18 component comes from that of the styrene dimer. For the styrene trimer, it seems to behave in the same way, even though we could not obtain a separate peak on gas-chromatogram.

Based on the above data, we can calculate the activation energy of the individual constituent. The activation energies of individual constituents were shown in Table 2, which were calculated from Arrhenius plots drawn based on their mass rate. The activation energies exceed 50kcal/mol for monomeric constituents, while less than 30kcal/mol for the non-monomeric constituent. We will lately refer to the difference of activation energies between monomeric and non-monomeric constituents in relation to the mechanism for PS thermal degradation.

Table 2 Activation energies based on the rate of individual constituents produced by thermal degradation of polystyrene

Component	Activation energy [kcal/mol]
Toluene	21
Ethyl benzene	26
Styrene (monomer)	56
α -Methyl styrene	17
1,3-Diphenyl propane	27
2,4-Diphenyl butene-1 (dimer)	63
nC ₂₅ (trimer)	76
Over all	50

Reactor content:

The reactor content is a brown solid at ambient temperature, but it melts at temperatures above 150°C. The reactor content of PS is more viscous than those of polyethylene and polypropylene. At degradation temperature it looks like boiling rice gruel. The properties of PS reactor content were also reported in the preceding papers [28, 38].

3.3 Mechanistic consideration

Since the earliest systematic works were carried out by Staudinger and coworker [1], a number of descriptions on the mechanism of PS thermal degradation can be found in the literatures [39, 41-44]. As a result, most of researchers seem to accept that PS thermal degradation proceeds through a free radical transfer mechanism initiated by random chain scission. The author also agrees with the free radical transfer mechanism in liquid phase that causes a random chain scission resulting in a molecular weight reduction of raw polymer during the thermal degradation of polystyrene.

However, in most of mechanistic considerations, researchers have not referred to the formation of non-monomeric constituents derived from PS thermal degradation. It is not possible to accomplish the consistency in the mechanistic consideration of PS thermal degradation without any referring to non-monomeric constituents, because the volatile product from PS invariably consists of monomeric and non-monomeric constituents. In the conventional radical transfer mechanism, there are various inconsistencies for the formation of monomeric and non-monomeric constituents derived from PS, as follows.

(1) As shown in Fig. 9, the difference in the activation energy between the polymerization and the depolymerization corresponds to the heat of polymerization. That is,

$$E_d = E_p + \Delta H_p \quad (3)$$

E_d : activation energy of depolymerization, E_p : activation energy of polymerization, ΔH_p :

heat of polymerization.

Correct data for E_p and ΔH_p of polystyrene are found in a handbook [45]. Substitution of 7.25kcal/mol for E_p and 17.1kcal/mol for ΔH_p to Eq.2 makes $E_d=24.4$ kcal/mol.

On the other hand, the observed activation energy of the formation of styrene in PS thermal degradation is 56kcal/mol as shown in Table 2 in this study (55kcal/mol in the previous work [38]). The difference in the activation energy between the formation of styrene in PS thermal degradation and the formation of styrene in PS depolymerization is significantly large enough to insist that they are different reactions.

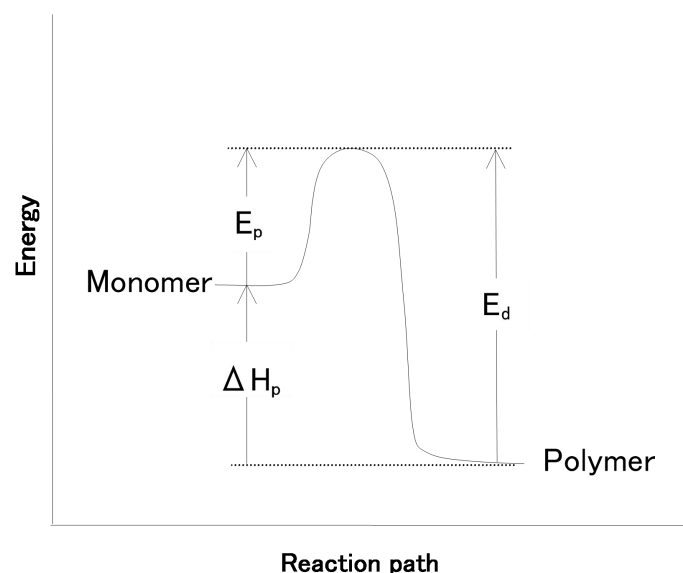


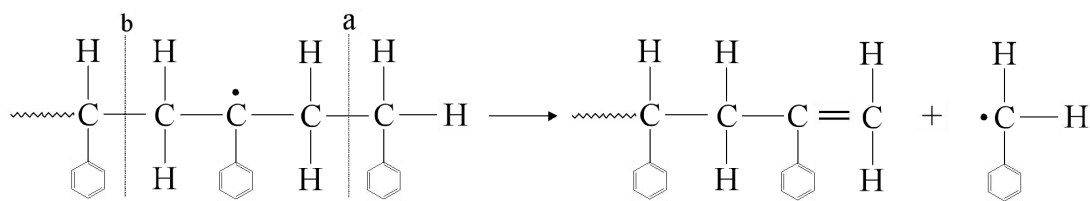
Fig. 9 Relationship between activation energies of polymerization and depolymerization

(2) Generally, we take it for granted that the formation of monomer in the thermal degradation of polymers is a reverse reaction of polymerization, that is, depropagation which proceeds by a free radical transfer mechanism resulting in the production of monomer. Even though a lot of non-monomeric components other than monomer are always involved in the thermal degradation of polymers.

PS is synthesized from a sole constituent of styrene. On the other hand, in PS thermal degradation a number of constituents, such as toluene, styrene, ethyl benzene, α -methyl

styrene, dimer, etc. are simultaneously formed. In the thermal degradation of PS, it is not valid to distinguish between the formation of styrene monomers and the formation of non-monomeric components. Therefore, the formation of styrene monomer does not appear to proceed solely by a different reaction, the reverse reaction of polymerization, rather than thermal decomposition. As PS is a macromolecule which consists of repeated units of styrene monomer, even if any small quantity of α -methyl styrene contaminates in styrene, such a mixture brings about a different polymer from PS. For the production of polystyrene, it is necessary for the reactant to consist of 100% of styrene. If the styrene is solely formed by a reverse reaction of polymerization in PS thermal degradation where a number of constituents are simultaneously generating in reactor, the concentration of styrene in degradation product has to approach to 100%, as the degradation temperature comes near to that of polymerization. But, with the lower temperature, the concentration of styrene monomer decreases, as shown in Fig. 8. That is, the formation of styrene in PS thermal degradation and the formation of styrene in PS depolymerization are not the same reaction.

(3) For example, toluene, a product of PS thermal degradation, is not a product derived from the propagation that consists of the release of monomeric fragments from primary or secondary radicals. If we apply the usual radical transfer mechanism to the formation of toluene, it proceeds through Reaction 1 shown as follows. That is, a methyl-phenyl radical formed by hydrogen abstraction and following β -cleavage of C-C bond (position **a**) shifts to toluene. The hydrogen abstraction is caused by an intermolecular radical transfer for the third carbon from chain-end. It brings about styrene dimer, when the β -cleavage of C-C main chain occurs at the position **b** of Reaction 1.



Reaction 1

When D_a is the dissociation energy of the C-C bond at the position **a** and D_b at the position **b** in Reaction 1, respectively, we can say that D_a is larger than D_b . That is,

$$D_a > D_b$$

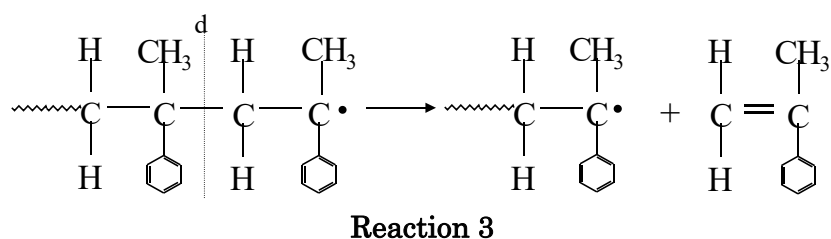
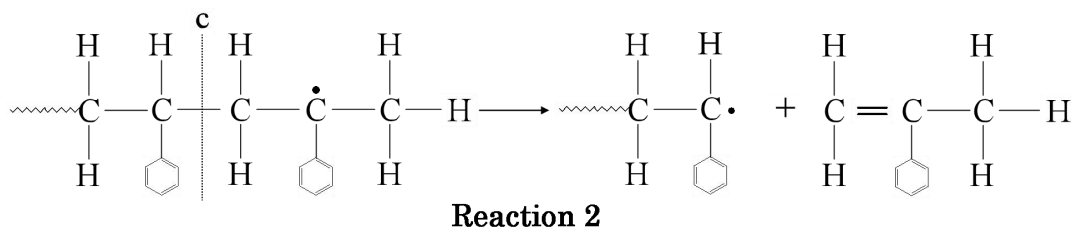
Meanwhile, as shown in Table 2, the observed activation energies of the formation of toluene and styrene dimer are 21 and 63kcal/mol, respectively. It conflicts with the above mentioned mechanistic conclusion that D_a is larger than D_b . Moreover the difference between the activation energy of the formation of toluene and that of styrene dimer is significantly large enough to insist that there is an inconsistency in the usual free radical transfer mechanism. For the formation of 1,3-diphenyl propane and trimer, we can also obtain a similar conclusion.

(4) If we apply the usual free radical transfer mechanism to the formation of α -methyl styrene in PS thermal degradation, it proceeds through Reaction 2 shown as follows. Reaction 2 resembles Reaction 3 (depropagation of poly- α -methyl styrene). When D_c is the dissociation energy of the C-C bond at the position **c** in Reaction 2 and D_d is the dissociation energy of the C-C bond at the position **d** in Reaction 3, respectively, we can say that D_c is larger than D_d . And the difference between D_c and D_d is estimated about 3kcal/mol [46]. That is,

$$D_c > D_d$$

The activation energy of the formation of α -methyl styrene in PS thermal degradation is 17kcal/mol as shown in Table 2. On the other hand, the activation energy of the formation of α -methyl styrene in the thermal degradation of poly- α -methyl styrene was reported to be 55kcal/mol by S. L. Madorsky [26]. Besides poly- α -methyl styrene yields 95-100% of

monomer (α -methyl styrene) during the thermal degradation in the temperature range of about 300-500°C [47].



Obviously those experimental results conflict with the above mentioned mechanistic conclusion that D_c is larger than D_d . Moreover the difference of 38kcal/mol between the activation energy of formation of α -methyl styrene experimentally obtained by Reaction 2 and the one similarly experimentally obtained by Reaction 3 is significantly large enough to insist that there is an inconsistency in the usual radical transfer mechanism.

What does bring about such as inconsistencies? In relation to it, S.L.Madorsky mentioned the mechanism of the thermal degradation of polymers in his book, "Thermal Degradation of Organic Polymers" [26], as follows.

"For the gas-phase pyrolysis of ordinary paraffins in a closed system, Rice and Rice suggested a mechanism which involves the steps of formation of free radicals and abstraction of hydrogen by the radicals, a process which continues until equilibrium sets in [48]. Simha et al. proposed a similar mechanism to explain the process of thermal degradation of polyolefins and other polymers [4, 5]. This mechanism involves several steps. ----"

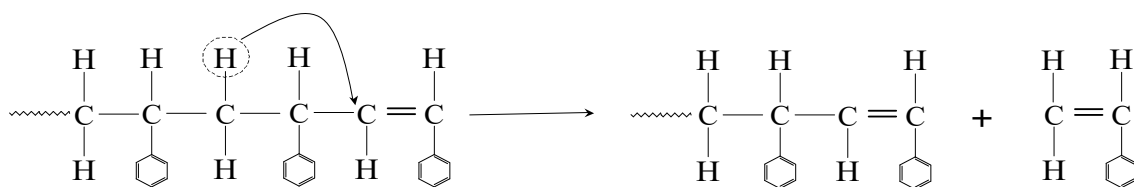
It could be presumed that Simha et al. proposed a mechanism similar to the gas-phase

pyrolysis of ordinary paraffins for the thermal degradation of polymers without well-grounded consideration. None of researchers have referred to the reaction system generating the thermal degradation of polymers other than S. L. Madorsky. Most of researchers have tacitly understood that the thermal degradation of polymers occurs in a homogeneous phase of liquid. But the reaction system generating the thermal degradation of polymers is not the same one generating the gas-phase pyrolysis of ordinary paraffins. In the reaction system generating the thermal degradation of polymers, there always coexist gas (volatile products) and liquid (reactor content) in the working reactor. Therefore, the formation of volatile products during the thermal degradation of polymers is a heterogeneous reaction in which the reactant is in a liquid phase and the product is in a gas phase as mentioned above and in the preceding papers [28, 29].

The above discussion shows that the radical transfer mechanism alone cannot explain the entire process of thermal decomposition of polymers. We essentially need a new concept for the generation of the volatile that is consistent with the observed fact.

4. The chain-end scission accompanying a hydrogen transfer for generating the volatile

When the experimental findings are in conflict with the radical transfer mechanism in the mechanistic consideration of the thermal degradation of polymers, we do not have any alternative other than the hydrogen transfer mechanism. For the decomposition of polystyrene, Staudinger et al. proposed a mechanism involving the hydrogen transfer at cleavage sites that produces one unsaturated end and one saturated end [1]. It is accompanied primarily by intramolecular hydrogen transfer at the site of scission. Jellinek also mentioned a hydrogen transfer mechanism which splits off monomer units, as shown below [49].



In this study, the author extend the hydrogen transfer mechanism to include the formation of non-monomeric compounds as well as monomeric compounds, as mentioned below.

The thermal degradation of mixed polymers suggests us that the random scission of C-C links of macromolecule is an intermolecular reaction accompanied with a free radical transfer [50]. When the random scission of main chain is accompanied with intermolecular radical transfer, there are two possible sources of available hydrogen atoms, the hydrogen atom from a tertiary benzylic carbon and the hydrogen atom from the secondary aliphatic carbon. However, the former one is more reactive compared to the latter. These alternatives lead to four chain-end patterns of the newly formed chain-end, and the transferring radical molecule. That is, 4 patterns, such as ①~④ shown in Fig. 10, are possible for the chain-end, which generates volatile products at the gas-liquid interface during thermal degradation of polystyrene. The dotted line in Fig. 10 shows the position for the scission of C-C links, although the double bond will not split undoubtedly. As shown in Fig. 11, each structure with pattern ①~④ is further decomposed by the chain-end scission accompanied with the hydrogen transfer from position 'a' or 'b', that corresponds to β -hydrogen near side or far side, respectively from the chain-end.

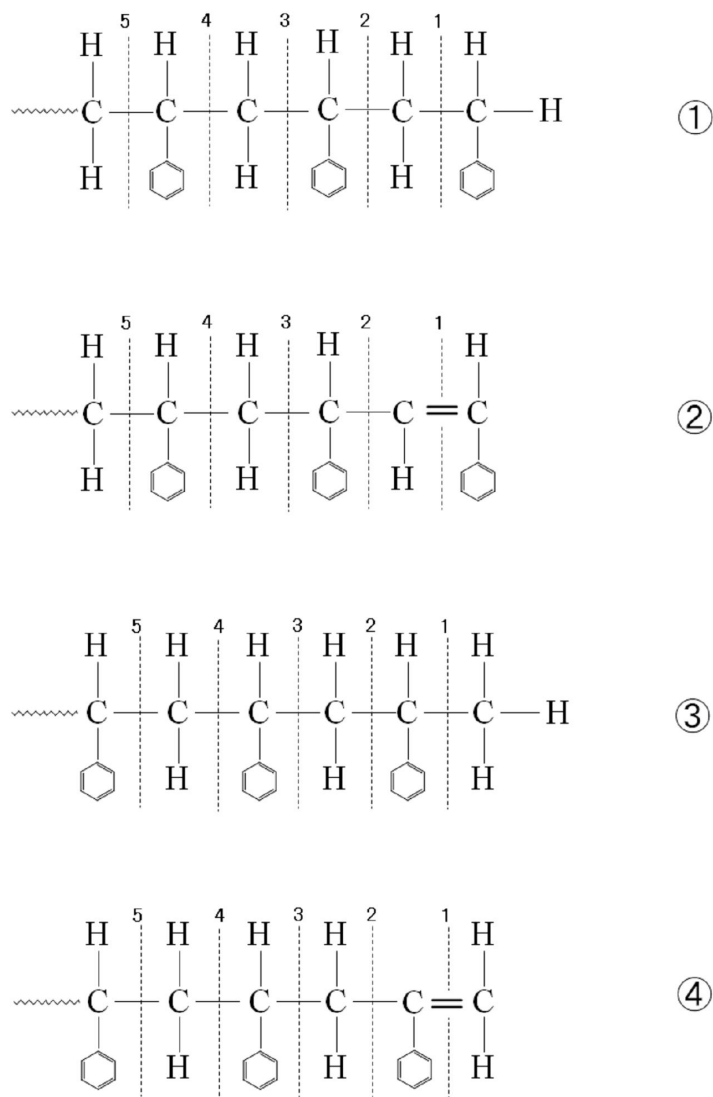


Fig. 10 Basic patterns of the chain-end during thermal degradation of polystyrene and the dotted line shows the position for scission

Fig. 11 shows a couple of examples of the chain-end scission accompanied with hydrogen transfer during the thermal degradation of polystyrene. When a chain-end scission occurs at the position 2 of pattern ① in Fig. 10, it produces styrene monomer or ethyl benzene according to a probability of which hydrogen is transferred from **a** or **b**. Here, we designate these reactions as ①-2-a (starting chain-end pattern: ①, position of scission: 2 and transfer of hydrogen: **a**) and ①-2-b, respectively. And when a chain-end scission occurs at the position 2 of pattern ②, it also produces styrene monomer. But there is not other choice of the hydrogen

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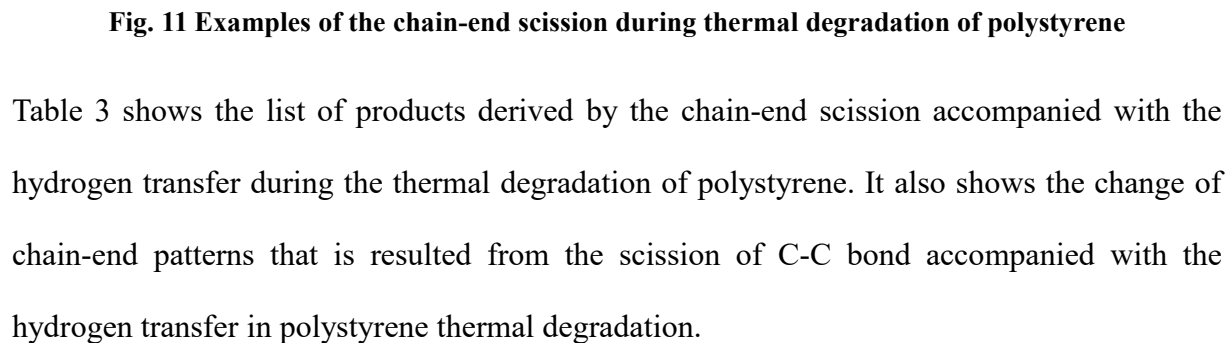


Table 3 List of products derived by the chain-end scission during thermal degradation of polystyrene

Starting chain-end	Position of scission	Transfer of hydrogen	Product	Change of chain-end	Resultant chain-end
①	1	b	Toluene	shift to	④
①	2	a	Styrene monomer	repeat	①
①	2	b	Ethyl benzene	shift to	②
①	3	a	1,3-Diphenyl propene	shift to	③
①	3	b	1,3-Diphenyl propane	shift to	④
①	4	a	Styrene dimer	repeat	①
①	4	b	1,3-Diphenyl butane	shift to	②
①	5	a	1,3,5-Triphenyl pentene-1	shift to	③
①	5	b	1,3,5-Triphenyl pentane	shift to	④
①	6	a	Styrene trimer	repeat	①
①	6	b	1,3,5-Triphenyl hexane	shift to	②
②	2	b	Styrene monomer	repeat	②
②	3	a	1,3 Diphenyl propadiene	shift to	③
②	3	b	1,3 Diphenyl propene	shift to	④
②	4	a	1,3-Diphenyl butadiene	shift to	①
②	4	b	Styrene dimer	repeat	②
②	5	a	1,3,5-Triphenyl pentadiene-1,4	shift to	③
②	5	b	1,3,5-Triphenyl pentene-1	shift to	④
②	6	a	1,3,5-Triphenyl hexadiene-1,5	shift to	①
②	6	b	Styrene trimer	repeat	②
③	1	b	Methane	shift to	②
③	2	a	Styrene monomer	repeat	③
③	2	b	Ethyl benzene	shift to	④
③	3	a	α -Methyl styrene	shift to	①
③	3	b	2-Phenyl propane	shift to	②
③	4	a	Styrene dimer	repeat	③
③	4	b	1,3-Diphenyl butene	shift to	④
③	5	a	2,4-Diphenyl pentene-1	shift to	①
③	5	b	2,4-Diphenyl pentane	shift to	②
③	6	a	Styrene trimer	repeat	③
③	6	b	1,3,5-Triphenyl hexane	shift to	④
④	2	b	Styrene monomer	repeat	④
④	3	b	α -Methyl styrene	shift to	②
④	4	a	1,3-Diphenyl butadiene	shift to	③
④	4	b	Styrene dimer	repeat	④
④	5	a	2,4-Diphenyl pentadiene-1,4	shift to	①
④	5	b	2,4-Diphenyl pentene-1	shift to	②
④	6	a	1,3,5-Triphenyl hexadiene-1,5	shift to	③
④	6	b	Styrene trimer	repeat	④

a: β -hydrogen near side from chain-end

b: β -hydrogen far side from chain-end

As shown in Table 3, when the monomeric styrene is formed by the chain-end scission accompanied with hydrogen transfer, it does not cause any change of the chain-end pattern. That is, the resultant chain-end has the same pattern as the starting chain-end before scission. And the same happens for the formation of styrene dimer and trimer. The author calls it “The rule of repeat for the monomeric constituent”. On the contrary, when the non-monomeric

constituent is formed, the resultant chain-end after scission invariably has a different pattern from the starting chain-end before scission. Moreover, it is not possible to form the original non-monomeric constituent from the resultant chain-end structure. Therefore, the formation of non-monomeric products is reduced compared to the formation of monomeric styrene, such as monomer, dimer and trimer which regenerate the same chain-end pattern. The above mentioned findings coincide with the observed result that the major products in thermal degradation of polystyrene is the monomeric constituent.

The structures resulted from the scissions of PS C-C links follow the L-s-L-s pattern of the main chain shown in Fig. 12, where 'L' stands for a large molecule ($\text{CH-C}_6\text{H}_5$) and 's' stands for a small molecule (CH_2). Thermal energy at the temperature of degradation leads to strains at various points of C-C chain, causing scissions. The larger molecules 'L' have more effect of anchor compared to the smaller ones 's', therefore the L-s bonds (as considered from the chain end) are easier to break compared to the s-L ones.

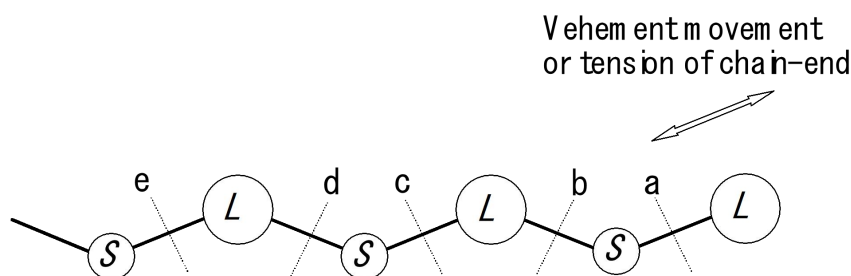


Fig. 12 Tendency for scission of C-C bond

There exist a couple of mechanistic principles for the chain-end scission accompanied with the hydrogen transfer in the thermal degradation of polymers. That is,

- The rule of repeat for the monomeric constituent
- The rule that L-s bonds are easier to break compared to the s-L ones

■ The steric hindrance for the hydrogen transfer

PS thermal degradation also follows the above mentioned principles. The non-steric hindrance explains the formation of toluene (nC8, 7.5 wt% of oils at 350 °C – Fig. 6) in a high amount by the reaction ①-1-b, though it generates the chain-end pattern ④ instead of the starting chain-end one ①. Contrary, the similar reaction ③-1-b leads to very few amount of methane (0.02wt% of volatile product). The ①-2-a and ①-3-b scissions are also favorable ones for the chain-end pattern ① and lead to formation of styrene monomer (with repeating chain-end pattern ①) and of 1,3-diphenylpropane at nC17 respectively. The latter generates the chain-end pattern ④.

The most important chain-end scission of pattern ② is ②-2-b that involves the vinylic bond which generates styrene monomer while repeating the same chain-end pattern. The ②-3-b scission leads to 1,3-diphenylpropene assigned to nC17 resulting to chain-end pattern ④.

Two reactions compete as most favorable ones for the scission of chain-end pattern ③, namely ③-2-b and ③-3-a. While the former one generates ethylbenzene (nC9) and chain-end pattern ④, the latter one, forming α -methylstyrene (nC10) and chain-end pattern ① has the advantage of a L-s type link and a more reactive H atom without steric hindrance. This might explain the formation of higher amount of α -methylstyrene compared to ethylbenzene. The ③-4-b scission leads to 1,3 diphenylbutane (nC17) and to chain-end pattern ④. The reaction ③-2-a leads to formation of styrene, however this is of less importance due to less reactive H atoms at primary carbon and partial steric hindrance of the phenyl group.

The chain-end ④ breaks down mainly by the ④-2-b scission that involves the weaker vinylic bond, leading to styrene monomer in a similar way to the ②-2-b scission. The ④-3-b scission leads to the formation of α -methylstyrene and of chain-end pattern ②. According to the L-s tendency for scission of C-C links in PS fragments, it is clear that the reaction ④-2-b is more favorable than the ②-2-b one. Also, this is more favorable than the reactions ①-2-a and

③-2-a, though both of them lead to styrene formation and repetition of chain-end pattern. Therefore we can consider the ④-2-b scission as the main process leading to formation of styrene monomer.

The process involving the repetition of same chain-end patterns is favored at higher temperature of degradation. On the contrary, the non-repeat mode of the chain-end pattern forces the production of non-monomeric compounds to decrease relatively with increasing temperature.

5. Conclusion

The conventional radical transfer mechanism mentioned in the literature has inherent insufficiencies and inconsistencies that the experimental findings are in conflict with. These facts show that the radical transfer mechanism alone cannot explain the entire process of the thermal degradation of polymers.

Those inconsistencies originate in the false understanding that the production of volatile proceeds in a homogeneous manner in liquid. In the polymer decomposition system generating the volatile product, there always coexist the gas (volatile product) and the liquid (reactor content) in the working reactor, where the chemical reaction takes a role of the rate controlling step. The formation of the volatile product in the thermal degradation of polymers is a heterogeneous reaction in which the reactant is in liquid phase and the product is in gas phase.

It could come to the conclusion that two distinct scissions simultaneously occur in the thermal degradation of polymers. One is the random chain scission that proceeds through the free radical transfer mechanism resulting in a molecular weight reduction of raw polymer in liquid phase. The other is the chain-end scission that proceeds through the hydrogen transfer

mechanism generating the volatile product at gas-liquid interface in the working reactor. Fig. 13 and 14 illustrate the above-mentioned mechanism for the thermal degradation of polymers.

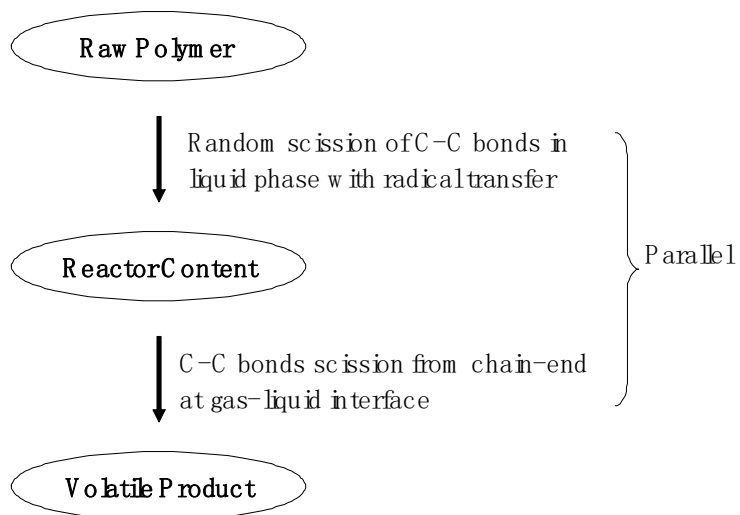


Fig. 13 Macroscopic mechanism for the thermal degradation of polymer

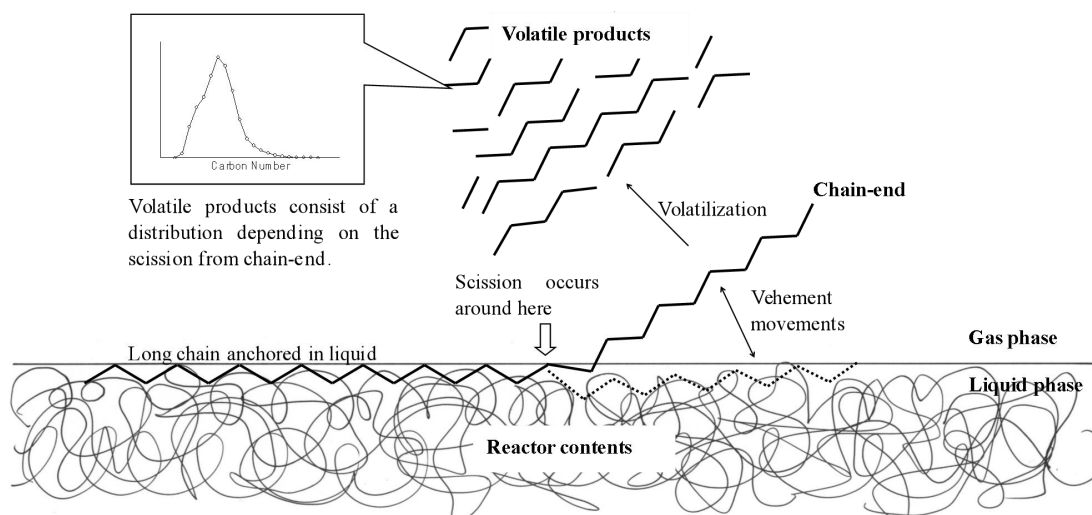


Fig. 14 Mechanism of the chain-end scission of polymer generating volatile products at gas-liquid interface proposed by K. Murata

All liquid products derived from the polymer emit a fluorescent color as shown in Fig. 15. The author is also aware of the possibility that the above-mentioned chain-end scission at gas-liquid interface could create two radical species, one is in a gas phase (volatile) and the other is in a liquid phase (reactor content). But it seems beyond the scope of this paper.

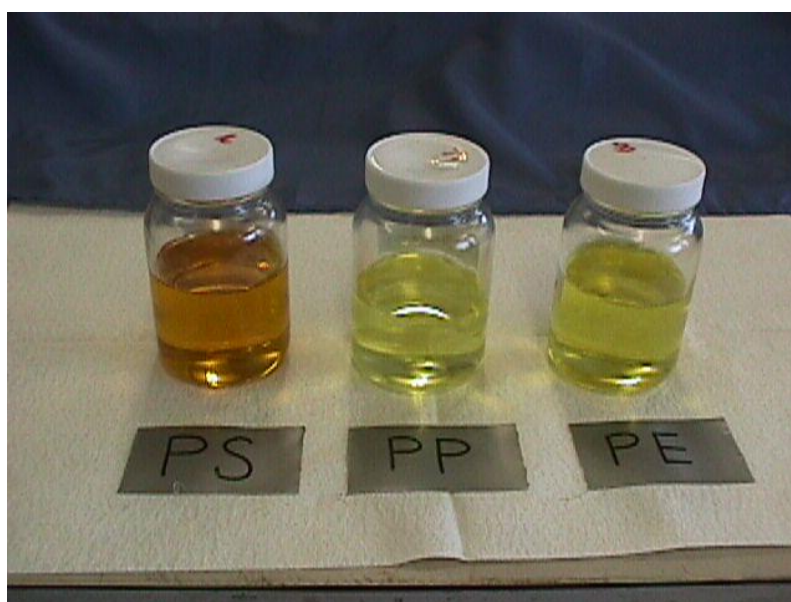


Fig. 15 The liquid product derived from PE, PP and PS

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