problem of the packing of two-dimensional polymer chains is very interesting, and comparisons with normal polymer solids will be helpful. It is still not clear that the packing of two-dimensional chains in one-layer is either islandlike or intertwined. These questions should be clarified in the future.

Registry No. 4,6-Dimethyl-2-propyl-1,3-dioxane, 5406-35-9.

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Photoinitiated Thermal Degradation of Polymers. 1. Elementary Processes of Degradation of Polystyrene

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ABSTRACT: Elementary processes of thermal degradation of polystyrene were studied at 160-270 °C by using a photoinitiation method with benzophenone derivatives. All the relative kinetic rate constants in thermal degradation of polystyrene except that for initiation were obtained by this new method. By putting the activation energy for depropagation ΔE_d = 24 kcal/mol, the activation energies for chain transfer (ΔE_f = 8 kcal/mol), back biting (ΔE_b = 12 kcal/mol), β-scission (ΔE_β = 24 kcal/mol), and termination (ΔE_t = 50 kcal/mol) were determined. The temperature range of the main-chain scission can be lowered from 300-320 °C of the usual thermal degradation condition to 160-200 °C of the photoinitiated case and the temperature range of monomer formation from over 300 °C to 230-250 °C. The ratio of trimer to monomer formed increases with decreasing temperature of the thermal degradation and becomes about a half at 230 °C.

Introduction

The thermal degradation of polystyrene has been a subject of study for many years.[1-4] At 270-300 °C, random main-chain scission[5,6] resulting in the decrease in molecular weight occurs due to the initiation by the thermal scission of the main-chain bonds and in some cases weak links such as head-to-head linkages, chain branches, chain end allylic bonds, and peroxide linkages.[7-9] At temperatures above 300 °C volatile products containing monomer and oligomers are formed[6,10-12] in addition to the random main-chain scission, and the half-weight-loss temperature after 30 min was reported to be 360 °C[1] for polystyrene in the absence of air.

A linear relationship between the half-weight-loss temperature after 30 min and the bond dissociation energy of the weakest bond in the main chain for various polymers[1,3] has shown that the initial step of the thermal degradation is the bond scission of the main chain into radicals and it has the highest activation energy. All the subsequent elementary reactions such as chain transfer, β-scission, etc, have much lower activation energies, and therefore it has been difficult to analyze clearly these elementary reactions at the thermal degradation temperatures.

The present series of work is based on the idea that if we replace this thermal initiation by a photochemical one, we would control the reaction temperature easily. In other words, by controlling the rate of radical production with photoinitiator and by carrying out the decomposition over a wide temperature range, we can observe rather easily the elementary reactions other than initiation. We can also avoid the difficulty of analyzing the kinetic data due to the possible contribution of the weak links to the degradation. Furthermore the photoinitiation method may be used in industry for recovery of degradation product, because the degradation temperature can be lowered and the species of the degradation products may be varied by changing the decomposition temperature. Photoinitiation may be carried out easily by using hydrogen abstraction with benzophenone derivatives. The photoinitiation mechanism of benzophenone for polystyrene degradation has already been clarified in solution.[13] In the present series of work, benzophenone derivatives with four or six

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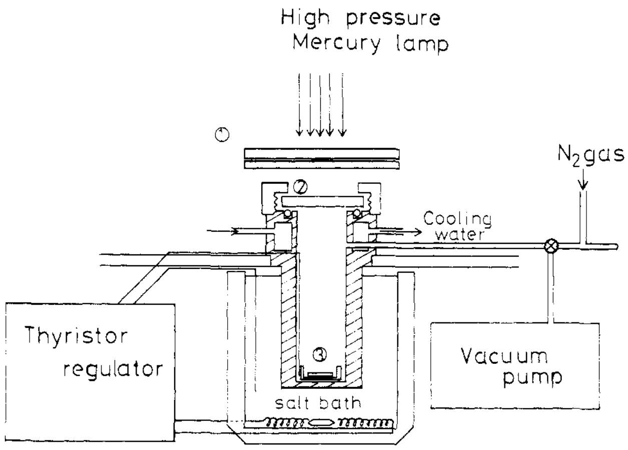


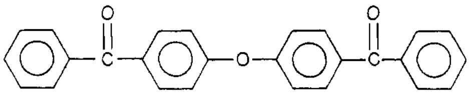
Figure 1. Schematic Diagram of apparatus for photoinitiated thermal degradation of polymers.

phenyl rings are used as photoinitiators in order to avoid the evaporation of initiator at high temperatures.

The present paper is concerned with the photoinitiated thermal degradation of polystyrene at 160–270 °C. Kinetic parameters such as rate constants and activation energies for elementary steps of polystyrene degradation are first obtained and discussed.

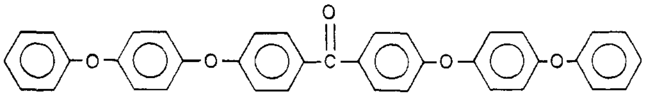
Experimental Section

Materials. Standard polystyrenes with narrow molecular weight distributions ($M_n = 1.0 \times 10^5, 3.3 \times 10^5, 9.0 \times 10^5$; $M_w/M_n \cong 1.1$) were purchased from Amuco Co. Most experiments were carried out with the samples having molecular weight of 3.3×10^5. Two benzophenone derivatives bis(4-benzoylphenyl) ether



diketone ether (DKE)

and 4,4′-bis[(4-phenoxyphenyl)oxy] benzophenone



tetraether ketone (TEK)

used as photoinitiators were kindly supplied from Adeca Argus Co. The former was used only at lower temperature where its volatilization during experiments is not important. Polystyrene films of 60–80-μm thickness containing 1.3×10^{-2} to 4.2×10^{-2} mol/L of photoinitiator were solvent cast onto a glass plate from dichloromethane solution.

Photoinitiated Thermal Degradation. Schematic illustration of the apparatus for photoinitiated thermal degradation are given in Figure 1. The film sample placed and sealed between two quartz plates was set at the bottom of the reaction vessel under the nitrogen atmosphere and was irradiated by 365-nm light from a 250-W ultrahigh-pressure mercury lamp (Ushio USH-250D) with glass filters (Toshiba UV29 and UVD36A). The reaction vessel was heated to 160–270 °C with a Supersalt M-2 type salt bath regulated by a thyristor regulater (Chino DR163). Actinometry was carried out with an International Light type IL-411T photoresist photometer calibrated by the potassium ferrioxalate/o-phenanthroline system.[13] The incident light intensity was $(1.5\text{–}6.8) \times 10^{-9}$ einstein·cm^{-2}·s^{-1} in the present experiments.

GPC Measurements. The changes in molecular weight and molecular weight distribution of polystyrene after the photoirradiation were measured by a TSK type HLC-802UR gel permeation chromatograph (GPC) with a GM1XH6 column and a UV (245 nm) detector in tetrahydrofuran at 40 °C. The calibration for GPC elution volume was carried out by using standard narrow molecular weight distribution polystyrene with various molecular weights. The amounts of monomer and trimer formation during the photoinitiated thermal degradation of polystyrene at 230–270 °C were measured by the same HLC-802UR GPC apparatus with a G200H8 column and a UV (254 nm) detector in tetrahydrofuran at 40 °C. No weight loss was observed for the samples sealed between two quartz plates.

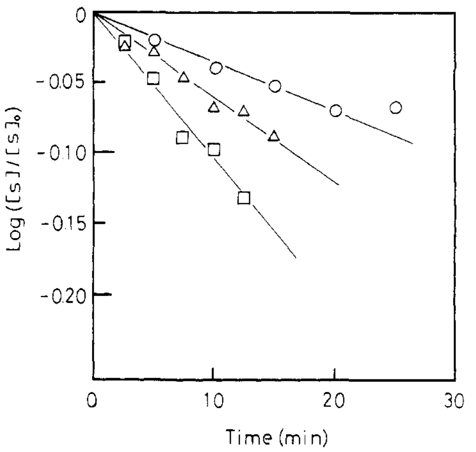


Figure 2. First-order plots of the change in the concentration of diketone initiator, [S], in polystyrene during photoirradiation at 160 °C (○), 180 °C (△), and 200 °C (□). $[S]_0 = 2.1 \times 10^{-2}$ (△) and 4.2×10^{-2} (○, □) base mol/L; $I_0 = 6.8 \times 10^{-9}$ einstein/(cm^2·s).

Measurements of Photoinitiator Disappearance. The changes in the concentration of aromatic ketone photoinitiators were measured by a JASCO type IR-G infrared (IR) spectrophotometer. The absorption band at 1650 cm^{-1} was used for determining the aromatic ketone concentration with an internal reference band of 1750 cm^{-1} for polystyrene absorption.

Results and Discussion

Photoinitiation Step of Degradation. The disappearance of photosensitizer (S) used for the photoinitiation of the degradation of polystyrene during 365-nm irradiation at 160–200 °C under the nitrogen atmosphere is shown in Figure 2. The aromatic diketone, DKE, and monoketone, TEK, were used as photosensitizers for experiments at 160–200 °C and at 200–270 °C, respectively. The rate of disappearance of the ketone increases with increasing temperature and obeys first-order kinetics with a decay constant which is proportional to the incident light intensity, I_0.

The primary processes for the decay of the aromatic ketone triplet ($^3S^*$) in the present system are given in the following:

$$S \xrightarrow{h\nu} {}^1S^* \rightarrow {}^3S^* \qquad (1)$$

$$^3S^* \xrightarrow{k_0} S \qquad \text{deactivation} \qquad (2)$$

$$^3S^* + PS \xrightarrow{k_q} S + PS \qquad \text{physical quenching} \qquad (3)$$

$$^3S^* + PS \xrightarrow{k_a} S^\bullet + P_c^\bullet \qquad \text{hydrogen abstraction} \qquad (4)$$

where $S^\bullet$ is the kethyl radical of S and $P_c^\bullet$ is the polystyrene on-chain radical. The rate of disappearance of aromatic ketone under the photostationary state is expressed by

$$\frac{d[S]}{dt} = k_a[PS][^3S^*] = \frac{k_a[PS] \times 10^3 I_0(1 - 10^{-\epsilon[S]l})/l}{k_0 + k_q[PS] + k_a[PS]} \cong \Phi \times 2.3 \times 10^3 I_0 \epsilon[S] = \alpha[S] \qquad (5)$$

where Φ is the quantum yield of ketone disappearance, I_0 is the intensity of incident light in einstein·cm^{-2}·s^{-1}, ϵ is the molecular extinction coefficient in M^{-1}·cm^{-1}, l is film

Table I
Quantum Yield for Ketone Disappearance, Φ, for Photoinitiated Thermal Degradation of Polystyrene

temp, °C	$[\mathrm{S}]_0 \times 10^2$, base mol/L	$I_0 \times 10^9$, einstein/(cm²·s)	Φ
160	2.1[a]	1.53	0.012
	4.2[a]	1.53	0.012
	4.2[a]	6.76	0.011
180	2.1[a]	1.53	0.020
	2.1[a]	6.76	0.020
	4.2[a]	1.53	0.021
200	4.2[a]	6.76	0.033
200	4.1[b]	6.76	0.0079
230	4.1[b]	6.76	0.016
250	4.1[b]	6.76	0.027
270	4.1[b]	6.76	0.038

[a] Diketone initiator (DKE). [b] Monoketone initiator (TEK).

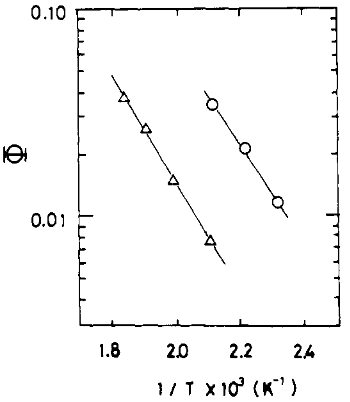


Figure 3. Arrhenius plots for quantum yields of initiator disappearance during photoinitiated degradation of polystyrene. Initiator: (△) TEK; (○) DKE.

thickness in cm, and the initiation rate parameter, α, is given by

$$\alpha = 2.3 \times 10^3 I_0 \epsilon \Phi \tag{6}$$

The approximation in eq 5 holds in the present system with $\epsilon[\mathrm{S}]l \ll 0.1$. The influence of disproportionation of the ketyl radical is disregarded in eq 5, because benzopinacol is mainly formed in the photolysis of benzophenone in benzene.[14] Equation 5 can be transformed to eq 7, showing the ketone concentration, [S], at time t

$$\ln([\mathrm{S}]/[\mathrm{S}]_0) = -2.3 \times 10^3 \Phi I_0 \epsilon t = -\alpha t \tag{7}$$

where $[\mathrm{S}]_0$ is the initial ketone concentration. The values of Φ calculated from the first-order plots of ketone disappearance as shown in Figure 2 with eq 7 are summarized in Table I. It is clear that at a same temperature the values of Φ are independent of initiator concentration and light intensity. The Arrhenius plots of Φ_s are given in Figure 3.

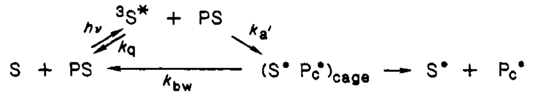
The quantum yield of the consumption of ketone, Φ, is of the order of 10^{-2}–10^{-1} with an activation energy of 10.5 kcal/mol for both aromatic ketones. As the rate of quenching of triplet benzophenone by polystyrene was ascertained to be much faster than the rate of hydrogen abstraction and much faster than the rate of natural decay[13,15] ($k_q[\mathrm{PS}] \gg k_a[\mathrm{PS}] \gg k_0$), Φ is given approximately by eq 8. Thus, the quantum yield, Φ, can be considered

$$\Phi = \frac{k_a[\mathrm{PS}]}{k_0 + k_q[\mathrm{PS}] + k_a[\mathrm{PS}]} \cong \frac{k_a}{k_q + k_a} \cong \frac{k_a}{k_q} \tag{8}$$

as the ratio of rate constant for hydrogen abstraction, k_a, to that for physical quenching, k_q, and the difference of activation energies for these rate constants, $\Delta E_a - \Delta E_q$, is supposed to be 10.5 kcal/mol. This value for $\Delta E_a - \Delta E_q$ is reasonable because ΔE_q was measured to be 2.3 kcal/mol[13] and ΔE_a is supposed to be 8–10 kcal/mol.[3]

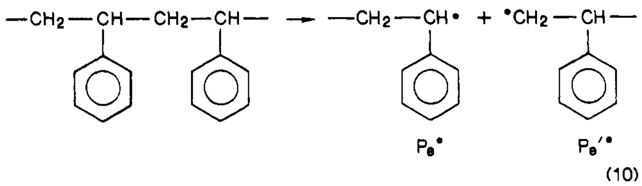
In our previous report,[16] we have shown that the hydrogen abstraction by benzophenone triplet from poly(vinyl alcohol) in solid film is a diffusion-controlled reaction and a strong cage effect reduces the apparent quantum yield of the reaction. But the reaction is no longer diffusion controlled above 120 °C, a temperature higher than the T_g of PVA by about 35 deg. The temperature range of the present experiment is much higher than the T_g of polystyrene, and furthermore, as is shown in Figure 3, there is no break in the Arrhenius plot of the quantum yield. These considerations support that the reaction can be considered as activation controlled, though the quenching reaction of benzophenone triplet by polystyrene is known to be diffusion controlled up to 140 °C.[17]

The possibility of cage disproportionation (k_{bw}) to give the initial ketone and polystyrene (eq 9) cannot be excluded in a solid polymer. But our previous work on poly(vinyl alcohol)[16] has shown that the backward reaction is not important at a much higher temperature than T_g. So, in the following, we disregard the cage backward reaction though the extent of the cage recombination is not known.



(9)

Elementary Steps of Degradation Other Than Initiation. Thermal degradation of polystyrene at 270–300 °C in the absence of air is known to be initiated by the chain scission at normal and weak links, producing polymer end radicals. For the case of thermolysis of a normal bond, two end radicals are produced (eq 10). The one is primary ($\mathrm{P_e'}^\bullet$) and the other is secondary ($\mathrm{P_e}^\bullet$), the former being more reactive than the latter. These end radicals may or may not result in more stable polymer on-chain radical, $\mathrm{P_c}^\bullet$, through chain transfer by hydrogen abstraction (eq 12). In the case of photoinitiated thermal degradation of polystyrene the polymer on-chain radical, $\mathrm{P_c}^\bullet$, is produced through eq 4. The subsequent elementary processes for $\mathrm{P_c}^\bullet$ should be the same for both pure thermal degradation and photoinitiated thermal degradation, and possible reactions of polystyrene radicals are summarized as follows:



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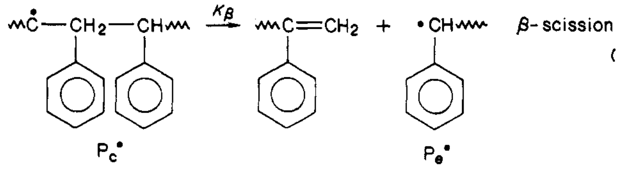

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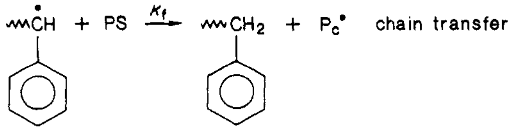

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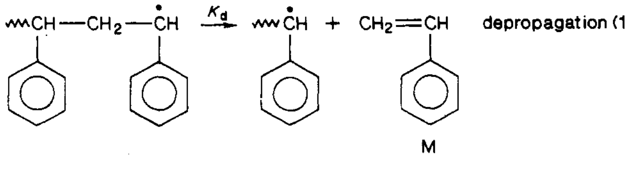

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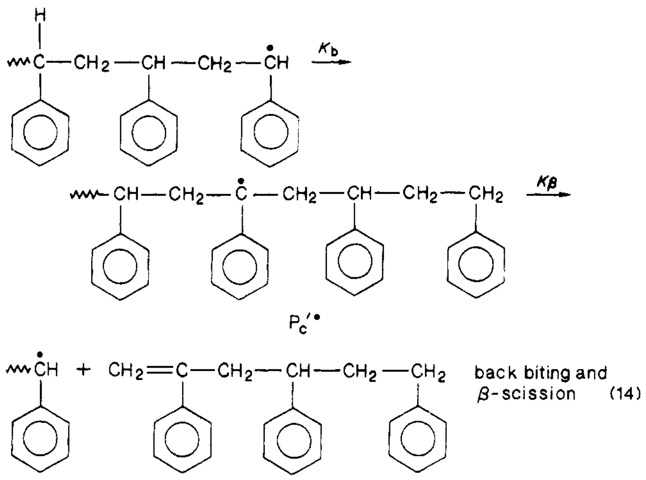

back biting and β-scission (14)

$$\left.\begin{array}{l} P^\bullet + P^\bullet \xrightarrow{k_{t1}} PP \\ P^\bullet + S^\bullet \xrightarrow{k_{t2}} PS \\ S^\bullet + S^\bullet \xrightarrow{k_{t3}} SS \end{array}\right\} \text{termination} \qquad (15)$$

Polymer on-chain radical, $P_c^\bullet$, undergoes β-scission (eq 11) resulting in polymer end radical, $P_e^\bullet$, which either depropagates (eq 13) or abstracts hydrogen intermolecularly (chain transfer, eq 12) reproducing $P_c^\bullet$ or intramolecular (back biting, eq 14) resulting in oligomers via special on-chain radical ($P_c'^\bullet$). Three types of temperature are considered in eq 158, where k_{t1} corresponds to termination between polymer radicals, k_{t2} termination between polymer and initiator radicals, and k_{t3} termination between initiator radicals.

The decrease in molecular weight of polystyrene during photoirradiation at 160–270 °C was followed by GPC. The typical increase in the number of main-chain scissions per monomer unit, Z_s, at 180 °C is shown in Figure 4. The Z_s was calculated by using eq 16, where $\overline{DP}_n$ is the number-average degree of polymerization and the subscript 0 means the initial value.

$$Z_s = \frac{1}{\overline{DP}_n} - \frac{1}{\overline{DP}_{n,0}} \qquad (16)$$

The results show that in the photoinitiated system the main-chain scission of polystyrene occurs at 160–200 °C which is more than 100 °C lower than the temperature of usual thermal degradation of polystyrene. The rates of main-chain scission of polystyrene at 180 °C with the present light intensities are about 100 times faster than the rate of thermal chain scission at 310 °C reported by Cameron et al.[5] Figure 4 also shows the square-root proportionality of scission rate on irradiation light intensity. The ratio of scission rate is 2.0 as compared to the square root of the ratio of light intensity 2.1, showing rather clearly the second-order termination between various radicals as is given by eq 15. This second-order termination is a normal behavior of the radicals, but it is not consistent with the first-order termination for the degradation of polystyrene at higher temperature proposed by some authors.[10]

In the case of photoinitiated thermal degradation, the rate of initiation, R_i, is equal to the rate of initiator disappearance (eq 5) and is given by

$$R_i = k_a[^3S^*][PS] \cong \Phi \times 2.3 \times 10^3 I_0 \epsilon[S] = \alpha[S] \qquad (17)$$

By using the stationary state assumption for intermediate radicals, the overall polymer radical concentration, $[P^\bullet]$ ($=[P_c^\bullet] + [P_c'^\bullet] + [P_e^\bullet]$), is expressed by

$$[P^\bullet] = \{k_{t1} + k_{t2}(k_{t1}/k_{t3})^{1/2}\}^{-1/2}(\alpha[S])^{1/2} = (\alpha[S]/\bar{k}_t)^{1/2} \qquad (18)$$

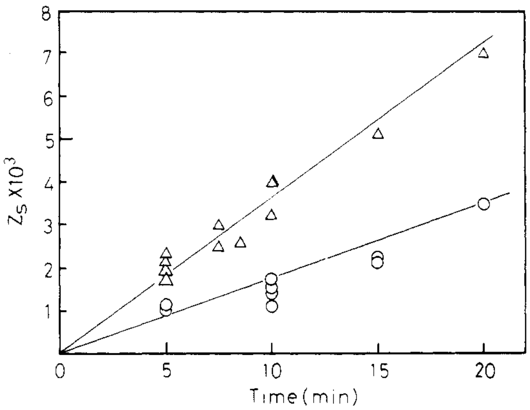

Figure 4. Change in the number of main-chain scissions per monomer unit, Z_s, during photoirradiation of polystyrene at 180 °C. $I_0 = 6.8 \times 10^{-9}$ (△) and 1.5×10^{-9} (○) einstein/(cm^2·s); $[S]_0 = 4.2 \times 10^{-2}$ base mol/L.

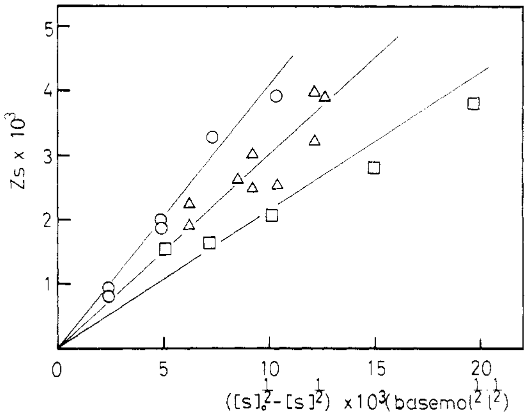

Figure 5. Plots of Z_s against $[S]_0^{1/2} - [S]^{1/2}$ for photoinitiated thermal degradation of polystyrene at 160 °C (○), 180 °C (△), and 200 °C (□). $I_0 = 6.8 \times 10^{-9}$ einstein/(cm^2·s); $[S]_0 = 4.2 \times 10^{-2}$ base mol/L.

where $\bar{k}_t = k_{t1} + k_{t2}(k_{t1}/k_{t3})^{1/2}$ is the reduced termination rate coefficient. When we express the concentration of two types of on-chain radicals and chain-end radical by

$$[P_c^\bullet] = r_1[P^\bullet] \qquad [P_e^\bullet] = r_2[P^\bullet] \qquad [P_c'^\bullet] = r_3[P^\bullet] \qquad (19)$$

with $r_1 + r_2 + r_3 = 1$, the parameter r_1 is derived to be

$$r_1 = \frac{k_f[PS]}{k_\beta + (\bar{k}_t\alpha[S])^{1/2}} \times \left[\frac{k_\beta}{k_\beta + k_b + k_f[PS] + (\bar{k}_t\alpha[S])^{1/2}}\right]\frac{(\bar{k}_t\alpha[S])}{k_\beta + (\bar{k}_t\alpha[S])^{1/2}} \qquad (20)$$

For the case that $(\bar{k}_t\alpha[S])^{1/2} \ll k_\beta, k_b, k_f[PS]$, eq 20 becomes to eq 21. This approximation holds in the present case;

$$r_1 \cong k_f[PS]/(k_\beta + k_b + k_f[PS]) \qquad (21)$$

since $\alpha[S]$ is 10^{-4}–10^{-5} mol·L^{-1}·s^{-1}, $\bar{k}_t$ is supposed to be smaller than 10^5 L·mol^{-1}·s^{-1} and k_β is probably of the order of 10^1–10^2 s^{-1}.[3] Then, from eq 18, 19, and 21 the rate of main-chain scission per monomer unit, dZ_s/dt, is given by

$$\frac{dZ_s}{dt} = \frac{k_\beta[P_c^\bullet]}{[PS]} = \frac{k_\beta k_f}{k_\beta + k_b + k_f[PS]}(\alpha/\bar{k}_t)^{1/2}[S]^{1/2} \qquad (22)$$

where the rate coefficient for back biting, k_b, can be ne-

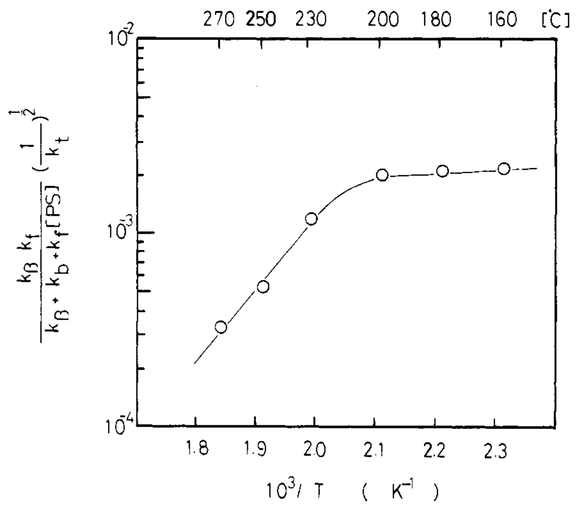

Figure 6. Arrhenius plots of the parameter $k_\beta k_f(k_\beta + k_b + k_f[PS])^{-1}\bar{k}_t^{-1/2}$ for the degradation of polystyrene.

glected for temperatures lower than 200 °C.

The integration of eq 22 by using

$$dZ_s/dt = (dZ_s/d[S])(d[S]/dt) = -\alpha[S](dZ_s/d[S]) \quad (23)$$

gives

$$Z_s = \frac{2k_\beta k_f}{k_\beta + k_b + k_f[PS]}\left(\frac{1}{\alpha\bar{k}_t}\right)^{1/2}([S]_0^{1/2} - [S]^{1/2}) \quad (24)$$

with the assumption that molecular weight dependence of k_{t1} does not influence much the constancy of $\bar{k}_t$, since the rate of diffusion-controlled polymer–polymer reaction (k_{t1}) would be much smaller than that of reactions containing small molecules (k_{t2} and k_{t3}). This will be ascertained later in Figure 11.

Equation 22 suggests that dZ_s/dt is proportional to $I_0^{1/2}$, which is already shown in Figure 4, and eq 24 suggests that Z_s is proportional to $[S]_0^{1/2} - [S]^{1/2}$ with the slope reciprocally proportional to $I_0^{1/2}$. Figure 5 ascertains the linear relationship of Z_s against $[S]_0^{1/2} - [S]^{1/2}$ for the experiments at 160–200 °C and shows that the slope corresponding to the number of chain scissions for a certain amount of initiator consumption decreases with the increase in degradation temperature. The same tendencies but with larger differences in the slopes were also observed at 230–270 °C. The reciprocal square root dependence on I_0 of the slope for the plots of Z_s against $([S]_0^{1/2} - [S]^{1/2})$ was ascertained at 180 °C.

The Arrhenius plot of the parameter $K = k_\beta k_f(k_\beta + k_b + k_f[PS])^{-1}\bar{k}_t^{-1/2}$ obtained from the values of α and the slopes for the plots of Z_s against $([S]_0^{1/2} - [S]^{1/2})$ is given in Figure 6. It consists of two linear parts with a break at the temperature a little higher than 200 °C. This can be best interpreted by the difference in the reaction conditions, i.e., whether the rate of chain transfer (k_f[PS]) is faster than the rate of β-scission (k_β) or vice versa. We know that the activation energy for β-scission is much larger than that for chain transfer though their exact values have never been determined. So it is not unreasonable to assume that the crossover of the two values occurs at around 200 °C. At temperatures lower than 200 °C, $k_f[PS] \gg k_\beta$ holds and K is reduced to be $k_\beta\bar{k}_t^{-1/2}[PS]^{-1}$, while at temperatures higher than 230 °C, $k_f[PS] \ll k_\beta$ holds, resulting in $K = k_f\bar{k}_t^{-1/2}$. Thus, the following values for the differences of activation energies were obtained

$$\Delta E_\beta - (1/2)\Delta E_t = -1 \text{ kcal/mol}$$

$$\Delta E_f - (1/2)\Delta E_t = -17 \text{ kcal/mol}$$

If we assume[3] $\Delta E_\beta \cong \Delta E_d$ = 24 kcal/mol, we get ΔE_t = 50 kcal/mol and ΔE_f = 8 kcal/mol. These values are first obtained in the experiments of polystyrene degradation. The value of ΔE_f = 8 kcal/mol is comparable to ΔE_f = 9.4 kcal/mol for the reaction of benzyl radical with cumene[3] and to ΔE_f = 13.3 kcal/mol for polystyryl radical with cumene.[18] The termination of polymer radicals in the molten system is a diffusion controlled reaction and the very high activation energy is not unreasonable. The only one estimated in the past is given by Melville et al.[19] and has a value of ΔE_t = 26 kcal/mol for poly(methyl methacrylate).

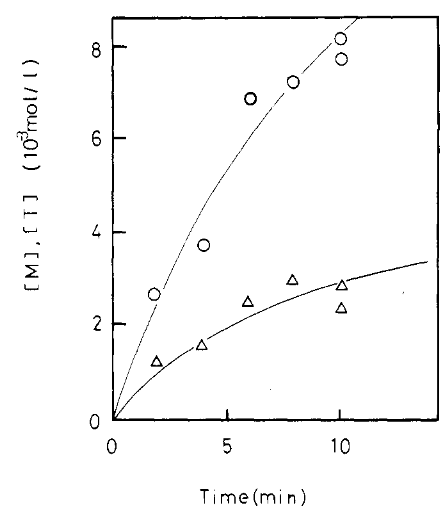

Figure 7. Formation of monomer (○) and trimer (△) during photoinitiated thermal degradation of polystyrene at 250 °C. I_0 = 6.8 × 10^{-9} einstein/(cm^2·s); $[S]_0$ = 4.1 × 10^{-2} mol/L.

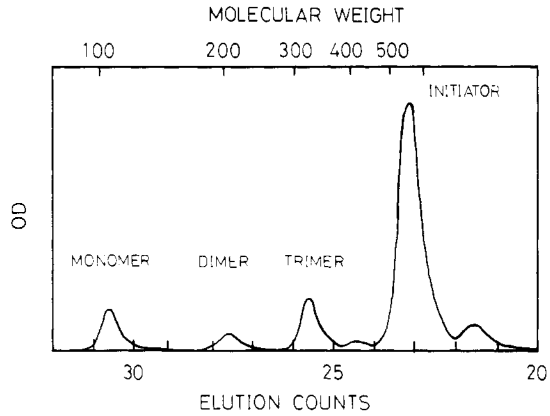

Figure 8. Typical GPC curve of low molecular weight reaction products for photoinitiated thermal degradation of polystyrene at 250 °C. I_0 = 6.8 × 10^{-9} einstein/(cm^2·s); $[S]_0$ = 4.1 × 10^{-2} mol/L.

Formation of Monomer and Trimer. The formation of monomer due to depropagation (eq 13) and trimer due to back biting and successive β-scission (eq 14) is usually observed at about 350 °C in the pure thermal degradation of aromatic polystyrene in the absence of air. But by using the technique of photoinitiation we can make these reactions occur at about 250 °C as is shown in Figure 7. The amounts of monomer, M, and trimer, T, of styrene formed during the photoinitiated thermal degradation at 230–270 °C were measured by GPC. A typical GPC chart in Figure 8 shows also the existence of dimer which would be produced by the β-scission of $P_c'^{\bullet}$ to the bond in the right side in eq 14. A small amount of tetramer is observed too. The rate of volatilization by photoinitiation at 250 °C in Figure 7 roughly corresponds to the rate of volatilization in pure thermal degradation at 320 °C.[5]

On the basis of reaction scheme given in the preceding section (eq 4 and 11–15) together with the stationary-state

Table II
Kinetic Parameters of the Degradation of Polystyrene

temp, °C	k_d/k_f, M	k_b/k_d	$10^3k_f/\bar{k}_t^{1/2}$, $M^{-1/2}/s^{-1/2}$	$10^3k_\beta/(\bar{k}_t^{1/2}[PS])$, $M^{-1/2}/s^{-1/2}$	$k_\beta/k_f[M]$	dZ_x/dZ_s
160			(10.0)	1.9	0.19	0.20
180			(5.2)	1.85	0.36	0.18
200			(2.3)	1.8	0.78	0.17
230	4.4	0.48	1.2	(1.75)	1.7	0.12
250	9.0	0.32	0.55	(1.7)	3.1	0.05
270	16	0.22	0.35	(1.65)	4.7	0.01
ΔE, kcal/mol	16	−12	−17	−1	16	
ΔE =	$(\Delta E_d - \Delta E_f)$	$(\Delta E_b - \Delta E_d)$	$(\Delta E_f - (1/2)\Delta E_t)$	$(\Delta E_\beta - (1/2)\Delta E_t)$	$(\Delta E_\beta - \Delta E_f)$	

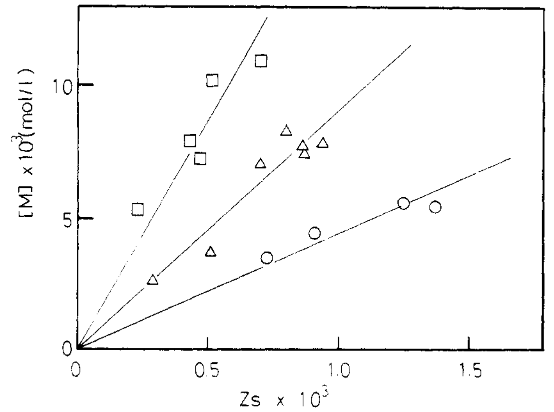

Figure 9. Plots of monomer formation, [M], against number of main-chain scission per monomer unit, Z_s, for photoinitiated thermal degradation of polystyrene at 230 °C (○), 250 °C (△), and 270 °C (□).

assumption, the rates of monomer and trimer formations are given by

$$\frac{d[M]}{dt} = k_d[P_e^\bullet] = k_d r_2[P^\bullet] = \frac{k_d k_\beta}{k_\beta + k_b + k_f[PS]}\left(\frac{\alpha}{\bar{k}_t}\right)^{1/2}[S]^{1/2} \quad (25)$$

$$\frac{d[T]}{dt} = k_\beta[P_c'^\bullet] = k_\beta r_3[P^\bullet] = \frac{k_\beta k_b}{k_\beta + k_b + k_f[PS]}\left(\frac{\alpha}{\bar{k}_t}\right)^{1/2}[S]^{1/2} \quad (26)$$

by using the same approximation of $(\bar{k}_t\alpha[S])^{1/2} \ll k_\beta, k_b, k_f[PS]$.

Then we get from eq 22, 25, and 26

$$d[M]/dZ_s = k_d/k_f \qquad d[T]/d[M] = k_b/k_d \quad (27)$$

or by integration eq 27 becomes to

$$[M] = (k_d/k_f)Z_s \qquad [T] = (k_b/k_d)[M] \quad (28)$$

The plots corresponding to the ratio given in eq 28 are shown in Figures 9 and 10. The ratio of monomer formation compared to the main-chain scission increases with increasing temperature (Figure 9) with an activation energy of 16 kcal/mol. This value corresponds to the activation energy difference, $\Delta E_d - \Delta E_f$, between the depropagation and chain-transfer processes. The ratio of trimer formation compared to monomer formation (Figure 10) increases with the decrease in temperature. This temperature dependence is caused by the activation energy difference, $\Delta E_b - \Delta E_d$, between the back biting and depropagation and suggests that at 230 °C trimer can be recovered up to 30% in volatile products, while its fraction is only several percent among volatile products at 350 °C in usual thermal degradation. Thus, in the case of photoinitiated degradation we can control the ratio of the amounts of products by changing the temperature. On the other hand, it is difficult to do so in pure thermal degradation because the degradation temperature can be scarcely varied.

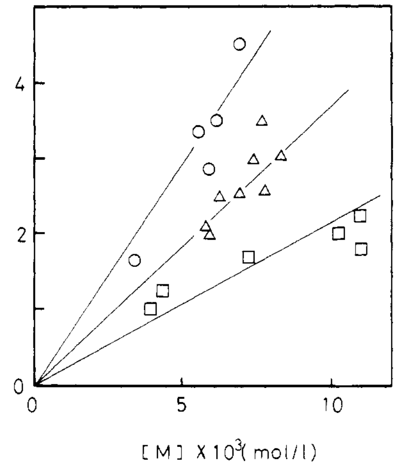

Figure 10. Plots of trimer formation, [T], against monomer formatin, [M], for photoinitiated thermal degradation of polystyrene at 230 °C (○), 250 °C (△), and 270 °C (□). $I_0 = 6.8 \times 10^{-9}$ einstein/(cm²·s); $[S]_0 = 4.1 \times 10^{-2}$ mol/L.

Table III
Scission Efficiency, $Z_s[PS]/\Delta[S]$; Zip Length, $[M]/Z_S[PS]$; and Product Ratio, [T]/[M], for the Degradation of Polystyrene

	$Z_s[PS]/\Delta[S]$	$[M]/(Z_s[PS])$	[T]/[M]
230 °C	4.6	0.44	0.48
250 °C	1.7	0.9	0.32
270 °C	0.87	1.7	0.22
	Extrapolation		
300 °C	0.3	4	0.12
350 °C	0.07	14	0.05

The kinetic data obtained in the present work are summarized in Table II in the form of the ratio of two rate constants in thermal degradation of polystyrene. The ratio $k_\beta/k_f[M]$ was calculated by using the extrapolated values of $k_f/\bar{k}_t^{1/2}$ and $k_\beta/\bar{k}_t^{1/2}$ from higher and lower temperature regions, respectively, given in parentheses in Table II. If an absolute value for only one of these rate constants were known, we could calculate the values for other kinetic constants. The same is true for the activation energies. The activation energy for depropagation was estimated to be 24 kcal/mol.[3] Then we get all other values as ΔE_f = 8 kcal/mol, ΔE_b = 12 kcal/mol, ΔE_t = 50 kcal/mol, and ΔE_β = 24 kcal/mol. In this case the value of ΔE_β = 24 kcal/mol has been derived without the assumption of $\Delta E_\beta \cong \Delta E_d$. The value of ΔE_b = 12 kcal/mol is quite reasonable because it is a hydrogen abstraction reaction by polystyryl end radical with an intramolecular six-member ring for-

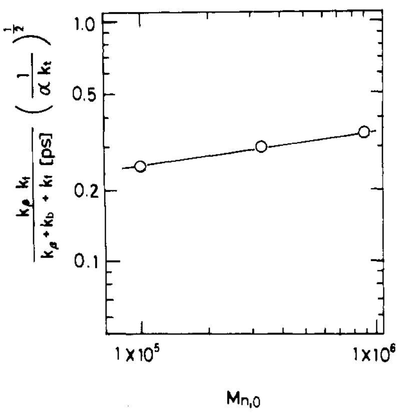

Figure 11. Effect of initial molecular weight $M_{n,0}$ on the slope of eq 24.

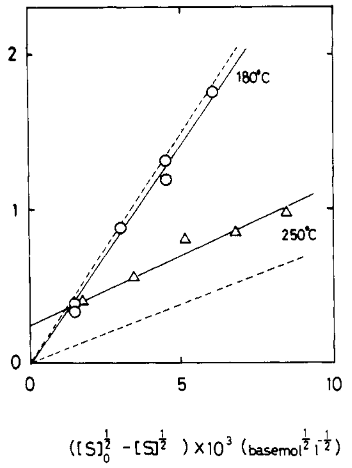

Figure 12. Plots of Z_s against $S_0^{1/2} - S^{1/2}$ for photoinitiated thermal degradation at 180 °C (○) and 250 °C (△) for polystyrene prepared by radical polymerization. Dotted lines correspond to the results for anionically prepared polystyrene.

mation similar to the chain-transfer reaction discussed in the preceding section.

In order to have a more concrete image of the present system, some modified parameters are given in Table III. The scission efficiency is the number of chain scissions per ketone molecule consumed. At lower temperatures, the values exceed unity, indicating that chain reaction cycle, i.e., β-scission, transfer, β-scission, transfer, etc., takes place before the termination of the radicals. The zip length is the number of monomer molecules former per terminal radical produced. This is small at the experiment temperatures but becomes very large at usual thermal degradation temperatures as expected. The ratio of the amount of trimer to that of monomer is about one to two at 230 °C and it decreases with increasing temperatures as already shown in Figure 10. It is to be noted that among the three parameters in Table III, the first and second ones depend on the initiation rate or the light intensity.

Subsidiary Problems in Photoinitiated Thermal Degradation of Polystyrene. Effect of Initial Molecular Weight of Polystyrene. The dependence of the slope for the linear relationship of Z_s against $[S]_0^{1/2} - [S]^{1/2}$ on the initial number-average molecular weight, $M_{n,0}$, of polystyrene is shown in Figure 11 for the photoinitiated thermal degradation at 180 °C with $I_0 = 6.8 \times 10^{-9}$ einstein/(cm^2·s). The supposed strong molecular weight dependence of k_{t1} ($k_{t1} \propto D_p \propto M_{n,0}^{-2.0}$) according to the reptation model[20] where D_p is the self-diffusion coefficient of polymer radical is not revealed explicitly in Figure 11, which suggests $Z_s \propto M_{n,0}^{0.15}$ and $\bar{k}_t \propto M_{n,0}^{-0.3}$. The contribution of the termination with initiator radical (k_{t2}) on $\bar{k}_t$ might result in the weak molecular weight dependence of $\bar{k}_t$.

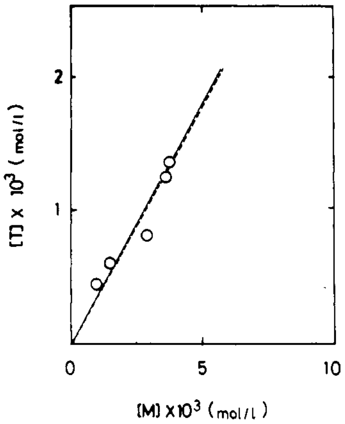

Figure 13. Ratio of trimer to monomer formation for radically prepared polystyrene degraded at 250 °C. Dotted line expresses the results for anionically prepared polystyrene.

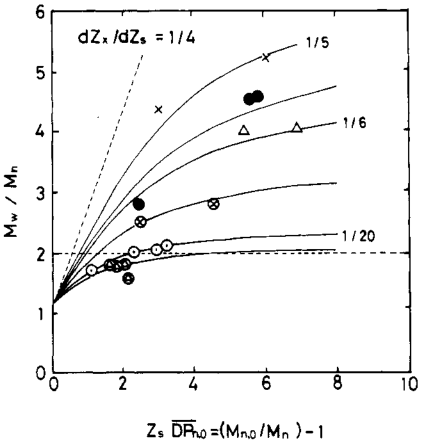

Figure 14. Change in molecular weight distribution during photoinitiated thermal degradation of polystyrene at 160 °C (×), 180 °C (●), 200 °C (△), 230 °C (⊗), 250 °C (⊙), and 270 °C (⊛). $M_{n,0} = 3.3 \times 10^5$; $M_{w,0}/M_{n,0} = 1.10$; $I_0 = 6.8 \times 10^{-9}$ einstein/(cm^2·s); $[S]_0 = 2.1 \times 10^{-2}$ M.

Degradation of Radically Prepared Polystyrene. The plots of Z_s against $[S]_0^{1/2} - [S]^{1/2}$ for photoinitiated thermal degradation of polystyrene prepared by radical polymerization are shown in Figure 12. Dotted lines correspond to the results for anionic polystyrene described already. The same slopes obtained for both radically and anionically prepared polystyrenes confirm that elementary steps of degradation other than initiation are not influenced by the existence of weak links supposed for radically prepared polystyrene. The chain scission at the very initial stage for radically prepared polystyrene degraded at 250 °C would be due to the initiation caused by weak links. The same ratio of monomer formation to trimer formation (Figure 13) was also observed for both radically and anionically prepared polystyrenes at 250 °C.

Change in Molecular Weight Distribution during Degradation. Figure 14 shows the change in molecular weight distribution as function of the extent of chain scission at various temperatures. The ratios of M_w to M_n do not converge to 2, the value to be expected for complete random chain scission, but they exceed it considerably especially at lower temperatures. The result shows that chain scission and cross-linking take place simultaneously, a phenomenon observed already for the photodegradation of polystyrene in solution at room temperature.[13] The ratios of the rate of cross-linking to that of chain scission,

dZ_x/dZ_s, at each temperature were estimated according to the procedure described already[13] by using eq 29–31

$$M_n = M_{n,0}/(1 + Z_s + Z_x) \tag{29}$$

$$M_w = \frac{2M_{n,0}\{Z_s - 1 + (1 + Z_s/\sigma)^{-\sigma}\}}{Z_s^2 - 4Z_x\{Z_s - 1 + (1 + Z_s/\sigma)^{-\sigma}\}} \tag{30}$$

$$\text{with} \qquad \sigma = M_{n,0}/(M_{w,0} - M_{n,0}) \tag{31}$$

relating M_w and M_n with Z_x and Z_s and are listed in Table II. Malhotra[6] also showed that M_w/M_n exceeds 2 for thermal decomposition of polystyrene below 330 °C.

The rate of cross-linking $d[Z_x]/dt$ and the rate of chain scission $d[Z_s]/dt$ both in $mol \cdot L^{-1} \cdot s^{-1}$ are given by

$$dZ_x/dt = k_{t1}[P^\bullet]^2 = k_{t1}\alpha[S]/\bar{k}_t \tag{32}$$

$$dZ_s/dt = [PS]\frac{dZ_s}{dt} = \frac{k_\beta k_f}{k_\beta + k_b + k_f[PS]}\left(\frac{\alpha}{\bar{k}_t}\right)^{1/2}[S]^{1/2}[PS] \tag{33}$$

At temperatures higher than 230 °C $k_f[PS] \ll k_\beta$ holds, and the ratio dZ_x/dZ_s reduces to

$$\frac{dZ_x}{dZ_s} = \frac{\bar{k}_t^{1/2}}{k_f[PS]}\frac{k_{t1}}{\bar{k}_t}(\alpha[S])^{1/2} \tag{34}$$

As all parameters other than $k_{t1}/\bar{k}_t$ were already obtained, we can estimate from eq 34 the ratio $k_{t1}/\bar{k}_t$. The value of $k_{t1}/\bar{k}_t$ was calculated to 0.23 at 250 °C, which gives $k_{t1}/k_{t3} = 0.026$ by assuming

$$\bar{k}_t = k_{t1} + k_{t2}(k_{t1}/k_{t3})^{1/2} \cong k_{t1} + (1/2)(k_{t1}k_{t3})^{1/2} \cong (1/2)(k_{t1}k_{t3})^{1/2} \tag{35}$$

with the approximation $k_{t1} \ll k_{t2} \cong (1/2)k_{t3}$.

The ratio of rate coefficient for polymer–polymer termination (k_{t1}) to that for termination between small radicals (k_{t3}) seems to be reasonable at 250 °C. However, this ratio increased with decreasing temperature, caused by the increase in cross-linking reaction at low temperatures as is shown by dZ_x/dZ_s in Table II. This suggests the existence of another mechanism of termination with low activation energies at low temperatures. As the chain transfer of polymer radical (k_f) becomes dominant at low temperatures owing to its low activation energy, the radical site might be able to move not by mass diffusion of a whole polymer molecule but though successive chain transfer, resulting in recombination. This reaction diffusion without mass transfer might be the reason of predominant occurrence of cross-linking in the degradation of polystyrene at low temperatures.

In conclusion, first of all, all the relative kinetic rate constants and activation energies during the thermal degradation of polystyrene were obtained by the photoinitiation method. They can be extrapolated to higher temperatures to estimate the values at usual thermal degradation temperatures of polystyrene. In the second, the temperature range of the chain scission can be lowered from 300–320 °C to the temperatures below 180 °C and the temperature range of monomer formation from 300 °C to 230–250 °C. In the last, the ratio of the amount of trimer to that of monomer produced can be controlled and it is larger at lower temperatures.

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Registry No. DKE, 6966-89-8; TEK, 115365-01-0; polystyrene, 9003-53-6.

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