Polymerization with Coupling Products of Stable Free Radicals

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POLYMERIZATION WITH COUPLING PRODUCTS OF STABLE FREE RADICALS

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ABSTRACT

   Poly(methyl methacrylate) and poly(styrene) terminated with a stable free radical such as 1,3,5-triphenylverdazyl or diphenylmethyl radical were prepared in order to obtain a polymer bearing a thermally labile bond at the ω-end. While preparation of the poly(methacrylate) terminated with the verdazyl was attempted by polymerization induced with the coupling product of the stable radical with the radicals from azo initiators, accumulation of the verdazyl resulted in low conversions of the monomer. The diphenylmethyl end group was introduced by primary radical termination with the diphenylmethyl radical from different sources. Although the desired end group was not introduced quantitatively, all the polymers except for poly(styrene) terminated with the verdazyl were confirmed to dissociate into the respective growing radicals on heating as evidenced by block copolymer formation. The thermally less stable character of the poly(methyl methacrylate)s terminated with the diphenylmethyl radical than the polymer prepared by polymerization with a conventional initiator indicate that the labile bond presenting at the terminus of the polymers facilitates thermal decomposition.

INTRODUCTION

   Radical polymerization that is a typical chain reaction has been used to obtain high polymers from a wide variety of monomers under mild conditions, even in

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aqueous media. Using a propagating radical as a chain carrier cannot usually be utilized for a desired reaction other than elementary reactions of radical polymerization because of the radicals quite short lifetime and extremely low concentration at the steady state. The iniferter technique proposed by Otsu et al. [1–3] consists of the reactions of a propagating radical with an additive. This has been called iniferter because it acts as an effective initiator and chain transfer agent or terminator simultaneously. Iniferter yields a radical with low or no initiation ability by cleavage of a labile bond or reaction with the propagating radical, leading to a thermally or photochemically dissociable bond at the terminus of the resulting polymer.

Generally, the propagating radical predominantly loses its activity by primary radical termination in the polymerization induced with initiators generating relatively stable radicals such as substituted diphenylmethyl radicals [4–8]. The polymers produced can be regarded as a coupling product of the stable free radical with the propagating radical, leading to the common structure of the monomer units between the initiator fragments. The radical polymerization induced with substituted tetraphenylethanes undoubtedly involves the substituted diphenylmethyl radical as the initiating and terminating radical. As a result, the polymers bearing the substituted diphenylmethyl moieties at the α- and ω-terminuses, and the bond between the ω-terminal monomer unit and the end group has been shown to be particularly thermally labile [9–12]. More recently, Rizzardo et al. [13–15] reported that di-*tert*-butyl nitroxide can be employed to quantitative trap the propagating radical to form a labile C—O bond, and the propagation has been confirmed to resume through cleavage of the C—O bond.

A stable free radical as an inhibitor can be used to measure the induction period, which is a typical technique used for determining the initiation rate. In an ideal case, the stable free radical quantitatively reacts with the primary radical to form an inactive product during the induction period, since no propagating radical can be formed. However, an increase in conversion was observed at the final stage of the induction period [16], and coupling of the polymer radical with the inhibitor may take place. We thought that propagation could compete with the scavenging reaction of a primary radical at a properly low concentration of the stable radical. If the bond dissociation is facilitated as the stability of the radicals increases, the coupling products of propagating radicals with a stable free radical used as scavengers could also have a thermally dissociable bond.

In the present study the coupling products of a stable free radical, 1,3,5-triphenylverdazyl (V·) [17], and the less stable diphenylmethyl radical (ϕ_2CH·) were chosen with the expectation that their coupling products could give polymers with thermally weak terminal bonds. Azodiphenylmethane (ADPM) was also used as the source of ϕ_2CH· to produce a polymer with an ϕ_2CH end group through primary radical termination. Block copolymer formation from polymers terminated with stable radicals was also examined.

EXPERIMENTAL

Materials

ADPM was prepared by oxidation of bis(diphenylmethyl)hydrazine [18]. V· was synthesized and purified as described in the literature [17]. Commercially avail-

able 2,2′-azobisisobutyronitrile (AIBN), 2,2′-azobis-2,4-di-methylvaleronitrile (AVN), and methyl 2,2′-azobisisobutyrate (MAIB) were purified by recrystallization.

$$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

AIBN

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

AVN

$$CH_3-\underset{\underset{H_3COOC}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$
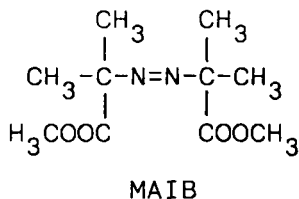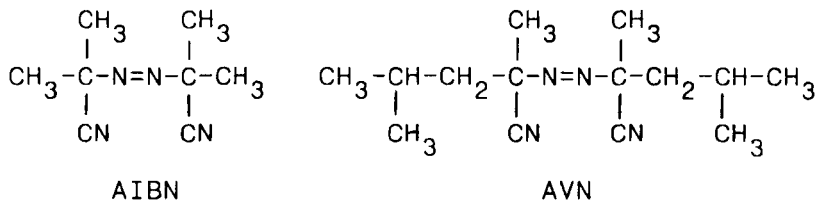
MAIB

Styrene (St) and methyl methacrylate (MMA) were distilled under reduced pressure before use.

Coupling Products of V·

After being bubbled with nitrogen, a benzene solution of V· containing an excess amount of AIBN or MAIB was heated at 80°C till it became colorless. The desired products were obtained by evaporation of the benzene [19]. The coupling product with the radical from AVN was prepared at 60°C.

Methyl 3,3-Diphenylpivalate

ADPM dissolved in benzene (10 wt%) was added in small portions to a benzene solution of MAIB at 10 minute intervals at 80°C. The reaction products obtained after evaporation of the benzene were rinsed with n-hexane. The diphenylpivalate was isolated in low yield from the n-hexane insoluble portion by passing the insoluble portion through a silica gel column eluted with benzene. It was recrystallized from n-hexane: mp 171°C. IR (KBr): 1720 (C=O); 1260, 1140, and 1120 (C—O); 760 and 690 cm^{-1} (aromatic C—H). ^{13}C NMR (CDCl$_3$): 24.56 (CH$_3$); 56.59 (quart. C); 51.75 (CH); 59.26 (CH$_3$O); 126–133 (aromatic 2-, 3-, and 4-C); 141.65 (aromatic 1-C); 177.86 ppm (C=O).

1,1,2-Triphenylbutane

The triphenylbutane was prepared by the reaction of methanol with the sodium salt of 1,1,2-triphenyl-1-butene in ether: mp 76.0–76.5°C. ^{1}H NMR (CDCl$_3$): δ = 0.64 (t, 3H, CH$_3$); 1.55 ppm centered (m, 2H CH$_2$); 3.04 (m, d, 1H, CH); 4.14 (d, 1H, CH), 7.17 centered (m, 15H, aromatic). ^{13}C NMR (CDCl$_3$): δ = 12.18 (CH$_3$); 27.92 (CH$_2$); 52.04 (CH); 58.57 (CH); 125.6–128.6 (aromatic 2-, 3-, and 4-C); 143.3–144.3 ppm (aromatic 1-C).

Polymerization and Block Copolymerization

Polymerizations initiated with the coupling products were performed in sealed tubes. For block copolymerization, ~0.3 g of the polymer and 4 mL of the second monomer were heated in a sealed tube at 80°C. From the polymer mixture formed, poly(St), poly(MMA), and the block copolymer were extracted with cyclohexane, acetonitrile, and benzene, respectively, by using a Soxhlet apparatus [20]. The compositions of the copolymers were calculated from the resonances due to the phenyl and methoxy protons in their ^{1}H-NMR spectra.

Measurements

Number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) calibrated with standard poly(St) were measured by a Toyosoda HLC 802UR high performance liquid chromatograph equipped with columns for gel permeation chromatography (GPC). Tetrahydrofuran was used as the eluent. The viscosity-average molecular weight ($\overline{M}_v$) of poly(MMA) was calculated from the intrinsic viscosity ([η] in dL/g) of a benzene solution measured by a Ubbelohde viscometer at 30°C using the following equation [21]:

$$[\eta] = 5.2 \times 10^{-4} M_v^{0.76}$$

^{1}H- and ^{13}C-NMR spectra were taken with Jeol NM PS-100 and a Jeol NM FX-60Q spectrometers, respectively. IR and visible spectra were recorded on Jasco A202 and Hitachi EPS-3T spectrophotometers. Thermogravimetric analysis (TGA) was performed by a Shimadzu TGA-20B thermobalance; ~1.5 mg of a polymer sample was heated in nitrogen atmosphere at 10°C/min.

RESULTS AND DISCUSSION

Dissociation of Coupling Product of V·

When the azo initiator (R—N=N—R) is allowed to decompose in the presence of V·, a coupling product (R—V) is formed [19]:
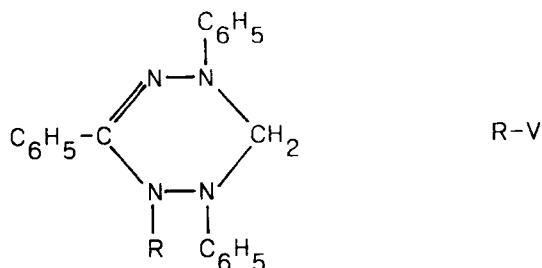
The disappearance of V· during this reaction was visually confirmed by the fading out of the color of the solution. The product isolated was found to dissociate into

V· and R· on heating [19]. On the basis of these facts, we anticipated that R· could initiate the polymerization and that V· could function as a terminator.
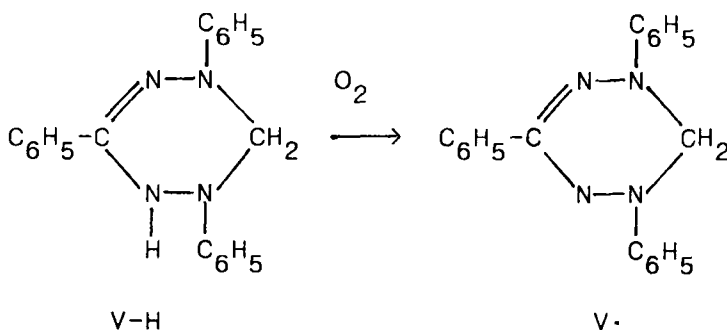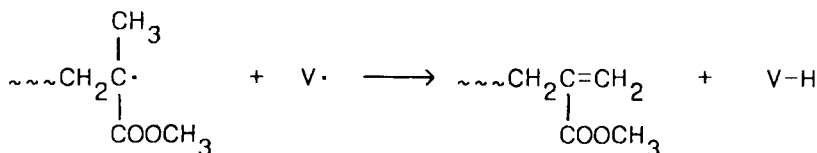
A colorless benzene solution of R−V (R = 2-cyano-2-propyl group) changed to green on heating, and absorbance at 720 nm increased with time according to first-order kinetics. The rate constants for the coloration were determined to be 3 × 10^{-7} and 9 × 10^{-6} s^{-1} at 60 and 100°C, respectively. Since the mutual coupling of R· could not be suppressed completely under these conditions, the 2-cyano-2-propyl radical generated could undergo mutual recombination in addition to the reaction with V·. The actual liberation rate of the radicals from N-(2-cyano-2,4-dimethylvaleryl)verdazyl seemed to be greater than the coloration rate. N-(2-Carbomethoxy-2-propyl)verdazyl provided faster coloration than N-(2-cyano-2-propyl)verdazyl.

Polymerization with R−V

Typical results of the homopolymerizations of MMA and St induced with various R−Vs are summarized in Table 1. Poly(MMA) and poly(St) were obtained in low conversions. The difference in the dissociation rates did not fully reflect the polymerization rates. The colorless polymerization mixture gradually changed to green during the polymerization of MMA, and polymer formation was suppressed after coloration. When the contents of the sealed tube were poured into a large amount of methanol to isolate the polymer, the color of the solution became deeper. This observation could be interpreted as oxidation of the colorless leucoverdazyl (V−H) to V· with air, since disproportionation between V· and the poly(MMA) radical could yield V−H.

$$\sim\sim\sim CH_2 \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot \quad + \quad V\cdot \quad \longrightarrow \quad \sim\sim\sim CH_2 \underset{\underset{COOCH_3}{|}}{C}{=}CH_2 \quad + \quad V{-}H$$

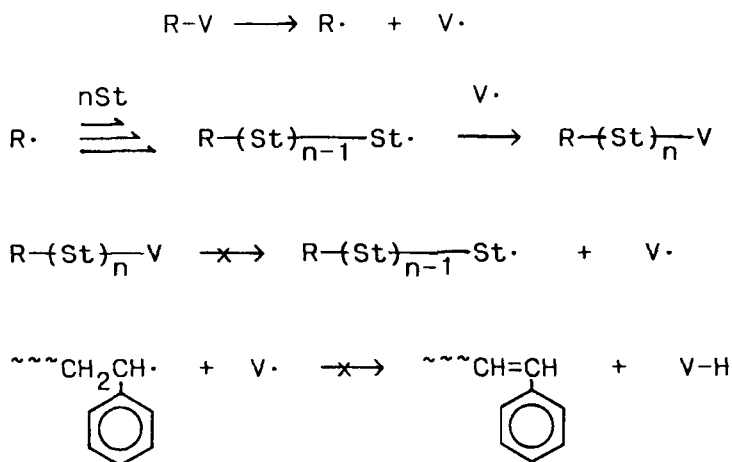V−H   V·

Contrary to the MMA polymerization, the polymerization mixture of St remained colorless after heating for 24 hours at 60°C. Moreover, the methanol solution of the polymerization mixture was still colorless in air, indicating that neither

TABLE 1.   Bulk Polymerization with the Coupling Product (R—V) at 60°C[a]

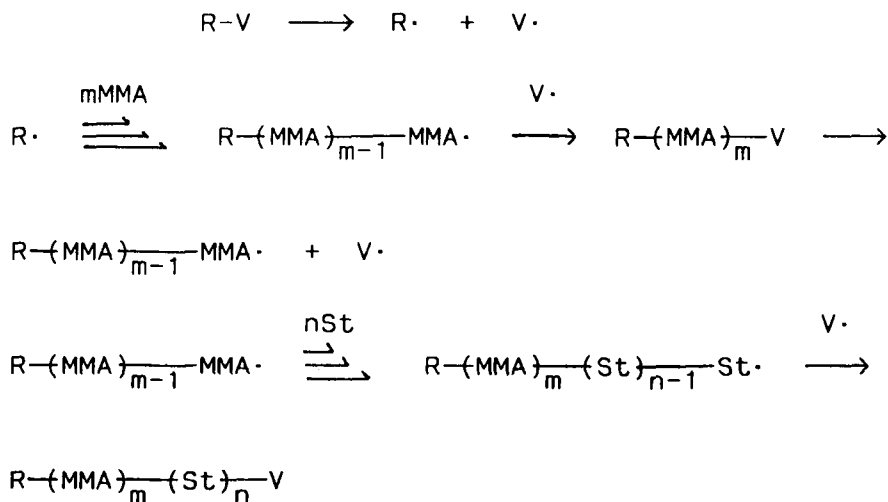| Monomer	R in R—V	Time, hours	Conversion, %	$\overline{M}_v$
MMA	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}$	29	4.4	1,740
MMA	$\overset{CH_3}{\underset{CH_3}{\Large{>}}}CHCH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}$	29	3.6	1,600
MMA	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}$	40	9.9	4,740
MMA	None	30	3.3	360,000
St	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}$	24	2.8	—
St	$\overset{CH_3}{\underset{CH_3}{\Large{>}}}CHCH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}$	24	5.3	—
St	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}$	24	8.4	—
St	None	24	2.8	—

[a][R—V] = 2 × 10^{-2} mol/L.

V· nor V—H was involved. The St polymerization with R—V can be presented by the following reactions.

$$R\text{--}V \longrightarrow R\cdot \;+\; V\cdot$$

$$R\cdot \overset{nSt}{\underset{\longrightarrow}{\rightleftharpoons}} \; R\text{--}(St)_{n-1}\text{--}St\cdot \;\overset{V\cdot}{\longrightarrow}\; R\text{--}(St)_n\text{--}V$$

$$R\text{--}(St)_n\text{--}V \;\xrightarrow{\;\;\times\;\;}\; R\text{--}(St)_{n-1}\text{--}St\cdot \;+\; V\cdot$$

$$\sim\sim\sim CH_2\underset{\bigcirc}{\overset{|}{CH}}\cdot \;+\; V\cdot \;\xrightarrow{\;\;\times\;\;}\; \sim\sim\sim CH{=}\underset{\bigcirc}{\overset{|}{CH}} \;+\; V\text{--}H$$

Since dissociation of R—V undoubtedly occurred to yield R·, the colorless polymerization mixture indicates a fast reaction of V· with the poly(St) radical to form a nondissociable C—N bond. Formation of V—H was not observed, and hydrogen abstraction with V· from the poly(St) radical was excluded.

After initiation followed by propagation, the poly(MMA) radical reacts with V· to form the labile C—N bond at the terminus as in ordinary bimolecular termination. The dissociation of the weak bond in the presence of a second monomer may afford a block copolymer, similar to the formation of a block copolymer by using iniferter [22].

$$R\text{--}V \longrightarrow R\cdot \;+\; V\cdot$$

$$R\cdot \overset{mMMA}{\underset{\longrightarrow}{\rightleftharpoons}} \; R\text{--}(MMA)_{m-1}\text{--}MMA\cdot \;\overset{V\cdot}{\longrightarrow}\; R\text{--}(MMA)_m\text{--}V \;\longrightarrow$$

$$R\text{--}(MMA)_{m-1}\text{--}MMA\cdot \;+\; V\cdot$$

$$R\text{--}(MMA)_{m-1}\text{--}MMA\cdot \overset{nSt}{\underset{\longrightarrow}{\rightleftharpoons}} \; R\text{--}(MMA)_m\text{--}(St)_{n-1}\text{--}St\cdot \;\overset{V\cdot}{\longrightarrow}$$

$$R\text{--}(MMA)_m\text{--}(St)_n\text{--}V$$

Relevant results of the block copolymerization initiated with poly(MMA) are given in Table 2. When V· and AIBN were used separately, the main sequence of reac-

TABLE 2.   Preparation of Block Copolymer from Poly(MMA) Terminated with V.[a]

| Poly(MMA)[b] | Time, hours | Conversion, % | | Block copolymer | | | |
		St	Poly(MMA)	Content, wt%	[St]/[MMA] (molar ratio)	Poly(MMA), wt%	Poly(St), wt%
1	10	6.0	0.9	6	—	41	53
2	10	3.2	45.2	26	13.4	31	43
3	24	10.4	41.0	44	3.4	16	40
4	24	10.6	29.9	32	5.1	18	50
5	24	6.0	53.1	39	8.8	13	48
6	24	6.9	45.5	45	3.9	13	42

[a]Heating poly(MMA), 0.30 g dissolved in St, 10 mL at 80°C.
[b]1: [AIBN] = 0.001 mol/L, 70°C. 2: [V·] = 0.02 mol/L, [AIBN] = 0.02 mol/L, 85°C. 3: [V−C(CH₃)₂CN] = 0.01 mol/L, [AIBN] = 0.017 mol/L, 60°C. 4: [V−C(CH₃)₂CN] = 0.01 mol/L, 60°C. 5: [V−C(CH₃)₂CN] = 0.03 mol/L, 60°C. 6: [V−C(CH₃)₂CN] = 0.01 mol/L, 60–70°C.

tions could be the formation of R—V followed by dissociation in the polymerization mixture, leading to poly(MMA). Dissociation of the terminal bonds of the polymers was found to take place on heating, and it yielded the block copolymer.

The resulting polymer mixture contained 25-45% of the block copolymer whereas the poly(MMA) prepared with AIBN without a labile bond gave a polymer mixture that included 5% of a block or graft copolymer after heating for 10 hours at 80°C. The efficiencies of the introduction of the labile bond and the initiation were not determined because of the concurrent thermal polymerization of St. Dissociation of the labile bond was proved by block copolymer formation.

Comparison of the GPC curves shown in Fig. 1 reveals that $\overline{M}_n$ was increased by block copolymer formation and that the increase in $\overline{M}_n$ due to the poly(St) block is greater than that of the original polymer. This tendency could be interpreted by slow termination in a viscous medium. A longer poly(St) block can also be expected from the compositions of the block copolymers shown in Table 2. Since the $\overline{M}_n$s of the homopolymers and the block copolymers were calibrated with standard poly-(St), the $\overline{M}_n$s of the block copolymers do not agree satisfactorily with estimates from the $\overline{M}_n$ of the original poly(MMA) and the composition.

Block copolymerization with the poly(St) initiated with R—V was also attempted under similar conditions in the presence of MMA as the second monomer.
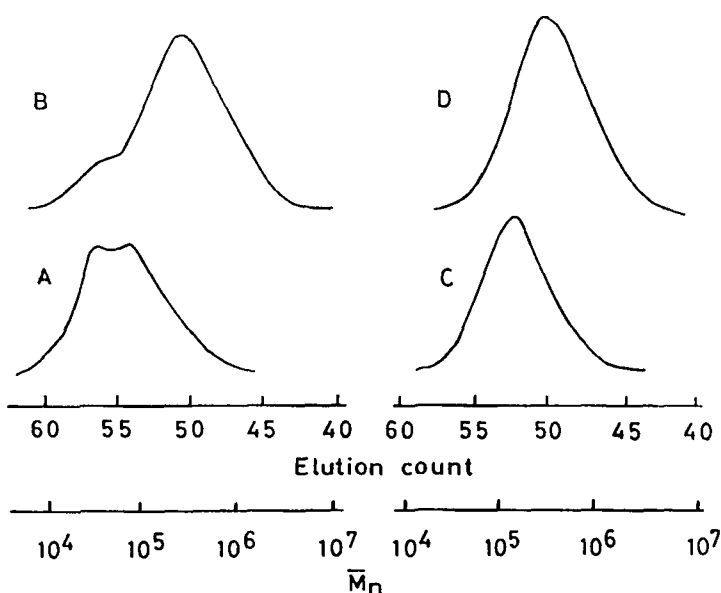

FIG. 1. GPC traces of poly(MMA) and block copolymer derived: A, poly(MMA) prepared with V—C(CH$_3$)$_2$CN (0.01 mol/L) and AIBN (0.004 mol/L) at 60°C, $\overline{M}_n$ = 52,800; B, MMA-St block copolymer from A at 80°C, $\overline{M}_n$ = 351,000, [St]/[MMA] = 3.4; C, poly(MMA) prepared with V—C(CH$_3$)$_2$CN (0.010 mol/L) and AIBN (0.0017 mol/L) at 80°C, $\overline{M}_n$ = 152,100; D, MMA-St block copolymer from C at 80°C, $\overline{M}_n$ = 369,800, [St]/[MMA] = 6.8
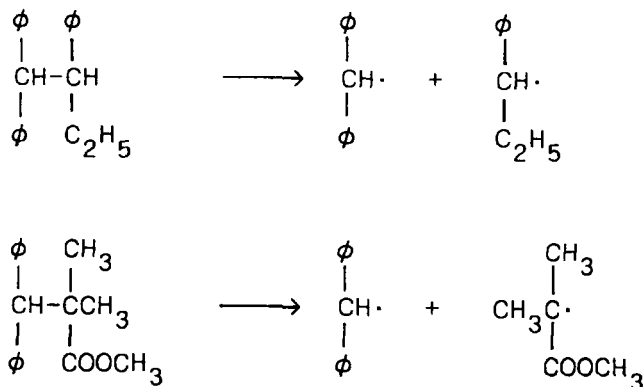
However, the recovered polymer mixture was found to consist of the homopoly-mers, poly(St), and poly(MMA). It is noted that the terminal bond of the former was reluctant to dissociate into the polymer radical and V· at 80°C. This finding seems to be consistent with the thermally stable character of the adduct of the verdazyl with a benzyl radical [19]. The effect of a subtle structural change on the thermal cleavage of the $C-C$ bond of the following tetrasubstituted ethanes has been reported [9].

$$
\begin{array}{cc}
\phi & CH_3 \\
| & | \\
\phi-C-\!\!\!-C-R \\
| & | \\
CN & COOCH_3
\end{array}
\qquad R = CH_3 \text{ and } C_2H_5
$$
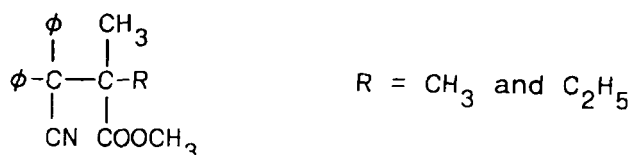
The polymerization rate of St in the presence of substituted ethane (R = CH_3) at 110°C was found to be quite similar to that of thermal polymerization. However, a substituted ethane with a larger substituent, such as R = C_2H_5, brought about faster polymerization of St. It is proposed that thermal scission of the $C-N$ bond to yield the poly(MMA) radical and verdazyl is facilitated by the internal strain arising primarily from the substituents bound to the quaternary carbon of the MMA unit and the substituents of the verdazyl.

Polymerization with Diphenylpivalate and Triphenylbutane

The main disadvantage of MMA and St polymerizations induced with $R-V$ was accumulation of V·, which was responsible for the low conversions shown in Table 1. To avoid this inexpediency, a less stable free radical, $\phi_2CH\cdot$, was chosen as a terminator and two types of coupling products ($R'-CH\phi_2$), methyl 3,3-diphenylpivalate ($R' = C(CH_3)_2COOCH_3$) and 1,1,2-triphenylbutane ($R' = CH(C_2H_5)C_6H_5$), were synthesized. These compounds were expected to decompose thermally as follows:

$$
\begin{array}{ccccc}
\phi & \phi & & \phi & \phi \\
| & | & & | & | \\
CH-CH & \longrightarrow & CH\cdot & + & CH\cdot \\
| & | & & | & | \\
\phi & C_2H_5 & & \phi & C_2H_5
\end{array}
$$

$$
\begin{array}{ccccc}
\phi & CH_3 & & \phi & CH_3 \\
| & | & & | & | \\
CH-CCH_3 & \longrightarrow & CH\cdot & + & CH_3C\cdot \\
| & | & & | & | \\
\phi & COOCH_3 & & \phi & COOCH_3
\end{array}
$$
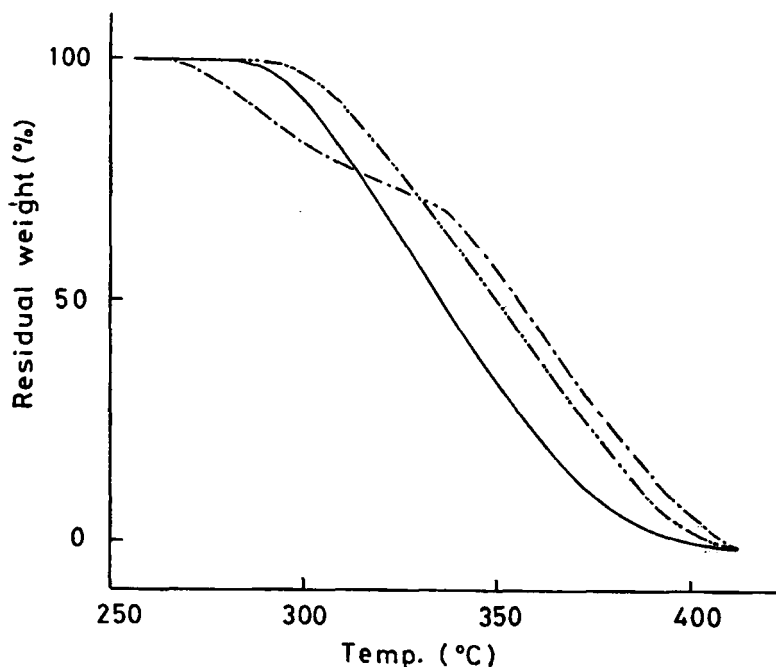
FIG. 2.   TGA curves of poly(MMA) prepared by polymerizations initiated with AIBN ($\cdot$-$\cdot$-), ADPM ($-\cdot\cdot-$), and methyl 3,3$'$-diphenylpivalate ($--$).

Since $\phi_2CH\cdot$ has been shown to participate in both initiation and termination by a kinetic study of vinyl polymerization initiated with ADPM [23], $R'-CH\phi_2$ was required to dissociate into $R'\cdot$ and $\phi_2CH\cdot$ for the present purpose. Preparation of the polymer with $R'-CH\phi_2$ or ADPM is expected to proceed through the following elementary reactions if primary radical termination is the main chain-stopping process.
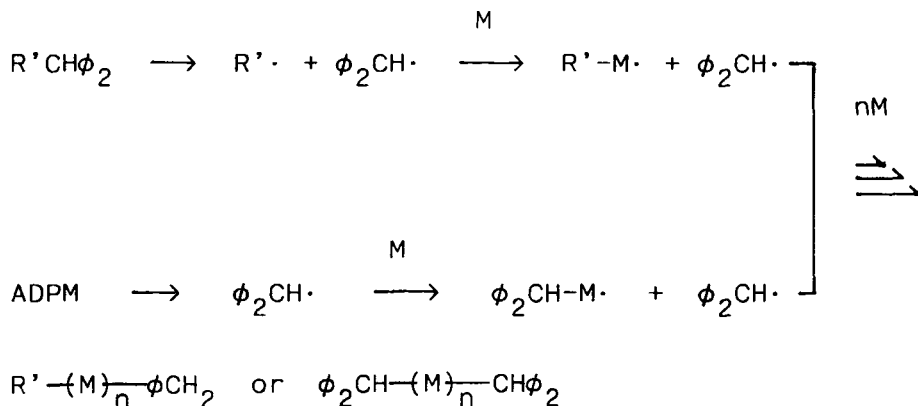
TABLE 3.   Bulk Polymerizations of MMA in the Presence and Absence of $R'-CH\phi_2$ at 100°C

$[R'-CH\phi_2] \times 10^2$ (mol/L)	Time, hours	Conversion, %	Rate, %/h
None	5.00	6.2	1.24
Pivalate, 7.76	1.67	14.7	8.80
Triphenylbutane, 7.76	1.67	3.5	2.10

TABLE 4. Preparation of Block Copolymer from Polymer Terminated with ϕ_2CH.[a]

Polymer	$\overline{M}_n \times 10^{-4}$	Time, hours	Monomer	Conversion, %		Fraction, wt%			$\dfrac{[St]}{[MMA]}$ (molar ratio)
				Polymer	Monomer	Poly (St)	Poly (MMA)	Block copolymer	
MMA[b]	50.1	10	St	39	3	1	36	63	0.1
MMA[c]	17.7	10	St	56	12	39	10	51	2.8
St[c]	5.5	7.7	MMA	74	10	7	51	42	0.4

[a]Heating 0.30–0.33 g of the polymer dissolved in 10 mL of the monomer at 80°C.
[b]Polymerized with the diphenylpivalate (0.077 mol/L) in benzene at 100°C.
[c]Polymerized with ADPM at 60°C.

$$R'CH\phi_2 \longrightarrow R' \cdot + \phi_2CH \cdot \overset{M}{\longrightarrow} R'-M \cdot + \phi_2CH \cdot$$

$$\left.\right] nM$$

$$\rightleftharpoons$$

$$ADPM \longrightarrow \phi_2CH \cdot \overset{M}{\longrightarrow} \phi_2CH-M \cdot + \phi_2CH \cdot$$

$$R' \cdot (M \cdot)_n \cdot \phi CH_2 \quad or \quad \phi_2CH-(M)_n-CH\phi_2$$
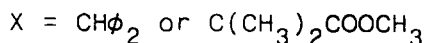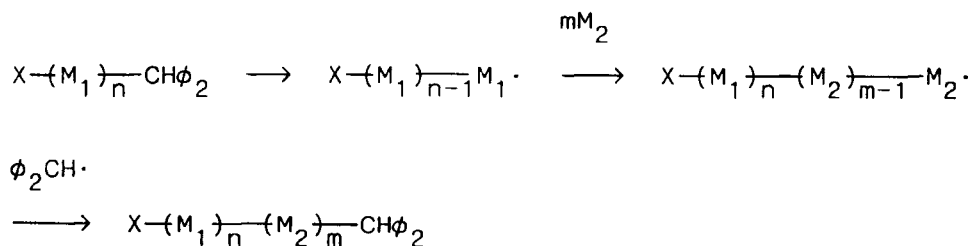
The polymerization of MMA was carried out at 100°C in the presence and absence of diphenylpivalate. As can be seen from Table 3, the faster rate of polymerization with pivalate by a factor of about 7 yielded the polymer, suggesting that poly(MMA)$-$CHϕ_2 could dissociate into the polymer and small radicals. Although the initiator reactivity of triphenylbutane, which is expected to generate ϕ_2CH$\cdot$ and 1-phenyl-1-propyl radical, is not as remarkable as that of pivalate, the radicals prepared by dissociation were scavenged with V$\cdot$ at 100°C. The apparent rate constant for the dissociation of tripheylbutane was of the order of 10^{-5} s^{-1} at this temperature.

Dissociation at the terminus of poly(MMA) was further confirmed by TGA. As shown in Fig. 2, degradation of the AIBN-initiated polymer started at about 260°C from the terminus with the unsaturated end group formed by disproportionation of poly(MMA) radicals (CH$_2$=C(COOCH$_3$)CH$_2-$). However, the polymers terminated with ϕ_2CH$\cdot$ exhibited faster degradation at 340°C or above than the polymer initiated with AIBN in which scission of the main chain starts degradation. These findings indicate that degradation of the polymer with the ϕ_2CH end group is faster than that initiated by cleavage of the main chain and slower than that where the bond is between the terminal unit and the unsaturated end group.

Block Copolymer from Polymer Terminated with ϕ_2CH$\cdot$

Poly(MMA) and poly(St) terminated with ϕ_2CH$\cdot$ from different sources were utilized for block copolymer formation.

$$X-(M_1)_n-CH\phi_2 \overset{mM_2}{\longrightarrow} X-(M_1)_{n-1}M_1 \cdot \longrightarrow X-(M_1)_n-(M_2)_{m-1}M_2 \cdot$$

$$\phi_2CH \cdot$$

$$\longrightarrow X-(M_1)_n-(M_2)_m-CH\phi_2$$

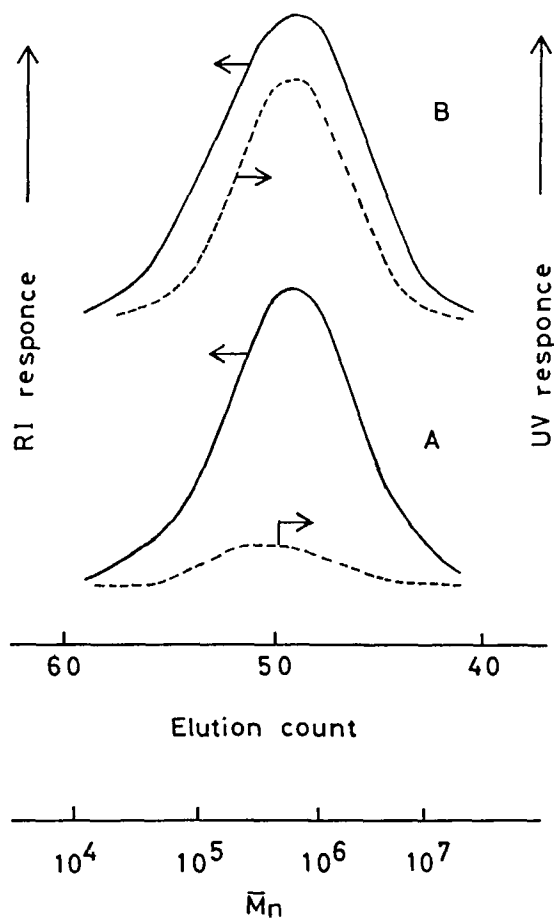$$X = CH\phi_2 \quad or \quad C(CH_3)_2COOCH_3$$

FIG. 3. GPC curves of poly(MMA) prepared with the pivalate (A) and the block copolymer (B): Monitored by differential refractive index (——) and UV absorption at 254 nm (- -).

The results are summarized in Table 4, where the polymers were prepared with the pivalate and ADPM accompanying primary radical termination. The formation of certain amounts of block copolymers indicates the presence of the ϕ_2CH group at the terminus and that the polymerization of the second monomer was initiated by the regenerated macroradical. The block copolymer from polymers initiated with ADPM consisted of a longer block from the second monomer, as already mentioned. However, the GPC curves in Fig. 3 reveal that $\overline{M}_n$ of poly-(MMA) initiated with pivalate, 8×10^5, was increased to 10^6 by block copolymerization, consistent with the small value for [St]/[MMA]. The much stronger UV response for the block copolymer was regarded as evidence for the presence of a poly(St) block. The same tendency was also observed in the GPC of some original polymers terminated with $\phi_2CH\cdot$ and the block copolymers from them. Apparently the stable radical behaved an efficient terminator, even in block copolymerization.

Poly(St) terminated with $\phi CH_2 \cdot$ also yielded poly(St-*b*-MMA), in accordance with thermal dissociation of triphenylbutane. Although thermal scission of the poly-(St)$-C\phi_2R$ bond at 100°C (when $R = OSi(CH_3)_3$) has been shown, poly(St) terminated with the phenoxydiphenylmethyl radical (ϕ_2CR, where $R = OC_6H_5$) could not initiate St polymerization [11]. On the basis of our observations, poly-(St)$-CH\phi_2$ can undergo homolysis at 80°G. Furthermore, initiation of St polymerization with triphenylbutane supports cleavage of the bond between the ω-end of poly(St) and the ϕ_2CH group.

CONCLUSION

ADPM and the coupling products of the $V \cdot$ or $\phi_2CH \cdot$ radical can be utilized with a sufficiently reactive radical to prepare poly(MMA) with thermally labile terminal bonds, although the presence of a stable free radical in high concentration suppresses the polymerization. Poly(St) terminated with $\phi CH_2 \cdot$ was also prepared by using ADPM or the coupling product. Poly(MMA) bearing the ϕ_2CH end group was thermally less stable than poly(MMA) prepared with AIBN. Block copolymers were produced by polymerization of a second monomer initiated by the macroradical generated from poly(MMA) and poly(St) with the dissociable bonds.

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