Thermal Degradation of Polyacetylenes Carrying Substituents

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ABSTRACT: Polyacetylenes with substituents were, in general, more thermally stable than polyacetylene in air. Their stability increased with increasing number and/or bulkiness of the substituents: $-[CH{=}C(n\text{-alkyl})]_n-$ < $-[CH{=}CPh]_n-$, $-[CMe{=}C(n\text{-alkyl})]_n-$ < $-[CH{=}C(t\text{-Bu})]_n-$, $-[CMe{=}C(SiMe_3)]_n-$ < $-[C(n\text{-alkyl}){=}CPh]_n-$, $-[CCl{=}CPh]_n-$. Among them, the polymers of aromatic disubstituted acetylenes were extremely stable (e.g., no oxidation or degradation in air at 160 °C after 20 h). The polymers from aliphatic disubstituted acetylenes were moderately stable at room temperature, while they easily degraded at higher temperature. None of these polymers underwent degradation in vacuo at 120 °C, which indicates that the oxidation process is essential to the thermal degradation. Products of polymer degradation in air contained appreciable amounts of oxygen. According to the thermogravimetric analysis of the polymers in air, the starting temperature of weight loss was as follows: $-[CH{=}C(\text{alkyl})]_n-$, ca. 150 °C; $-[CMe{=}C(n\text{-alkyl})]_n-$, ca. 200 °C; $-[CMe{=}CPh]_n-$ and $-[CCl{=}CPh]_n-$, ca. 300 °C.

Introduction

The chemistry and physics of polyacetylene have recently been the subject of intensive research.[1] This polymer, however, possesses difficulties, such as instability to air and insolubility in any organic solvents. According to the literature, polyacetylene readily takes up oxygen in air even at room temperature, leading to decomposition,[2,3] while it retains its weight below 320 °C under helium.[4]

On the other hand, only a few reports have appeared regarding the thermal stability of polyacetylenes with substituents because the preparation of such polymers is rather difficult: Polypropyne is as sensitive to air as polyacetylene[5] and thermally less stable than polyacetylene, as evidenced by the finding that its weight loss starts at about 150 °C under helium.[6] Poly(phenylacetylene) begins to lose weight at about 270 °C under nitrogen.[7] Poly(perfluoro-2-butyne) is stable, showing only a 10% weight loss at 525 °C in air.[8]

We have achieved the synthesis of various polyacetylenes with substituents by employing transition-metal catalysts exploited by us.[9] Unique and interesting properties of these polymers, such as gas permeability,[10] photoconductivity,[11] and radiation degradability,[12] have been described. These polymers appear to be reactive and therefore labile because of the presence of alternating double bonds along the main chain. It is hence interesting and also important for practical applications to elucidate the thermal stability of these polymers in air.

This paper reports on the stability in air, thermal degradation, and thermogravimetric analysis of polyacetylenes having substituents. The polymers studied are those from aliphatic or aromatic mono- and disubstituted acetylenes and Si-containing disubstituted acetylenes. The relationship between polymer structure and stability and the effect of oxygen on degradation have been revealed. The features and mechanism of the present degradation are discussed.

Experimental Section

Polymer Synthesis. Polymers of aliphatic, aromatic, and Si-containing acetylenes were prepared with Ziegler or group 5 and 6 transition-metal catalysts according to the methods described in the references cited in Table I. As Table I shows, the polymers were obtained in yields as high as 50–100% by the selection of suitable catalyst and polymerization conditions. Number-average molecular weights ($\bar{M}_n$) of polymers lie in the range of ca. 6×10^4 to 5×10^5.

Polymer Degradation. Polymer stability at room temperature was examined by allowing the polymer samples to stand in air for 3 months in the dark. For the thermal-degradation test, powdery polymers (ca. 15 mg each) were kept in open brown Erlenmeyer flasks at temperatures between 100 and 200 °C for a certain period of time. For comparison, control experiments under vacuum were done in well-degassed and sealed glass tubes.

Analyses. $\bar{M}_n$, weight-average molecular weights ($\bar{M}_w$), and polydispersity ratios ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) using a Jasco Triroter chromatograph (Shodex A802, A804, and A806 polystyrene-gel columns, eluent $CHCl_3$) on the basis of polystyrene calibration. IR spectra were recorded on a Shimadzu IR435 spectrophotometer. Elemental analysis was performed by the Laboratory for Organic Elemental Microanalysis, Kyoto University. Thermogravimetric analysis (TGA) was performed either in air or in a nitrogen atmosphere with a Shimadzu DT-20B thermal analyzer and Shimadzu TGC-20 thermogravimetric cell (sample size ca. 4 mg, heating rate 10 °C/min, maximum temperature 500 °C, flow rate of N_2 ca. 300 mL/min).

Results

Polymer Stability at Room Temperature. Table II shows data on the stability of polyacetylenes with substituents after leaving samples in air at room temperature for 3 months in the dark.

Poly(1-hexyne) and poly(isopropylacetylene), which are polymers of aliphatic monosubstituted acetylenes, are so unstable that they are easily oxidized and degraded in air at room temperature. This is demonstrated by the appearance of strong absorption bands due to C=O and OH groups in the IR spectra and by the remarkable reduction of their molecular weights.

Poly(phenylacetylene) and poly(2-alkynes) showed only slight molecular weight decreases and weak bands due to C=O and OH groups; thus they are stable to some extent at room temperature.

None of the polymers from *tert*-butylacetylene, the two Si-containing disubstituted monomers in Table II, and aromatic disubstituted acetylenes were oxidized or showed any molecular weight decrease. Consequently it can be said that they are stable at room temperature. This is important when these polymers find applications in air at room temperature.

There are two trends in the above results: (i) polymers of disubstituted acetylenes usually possess higher stability than those of monosubstituted acetylenes; (ii) polymer stability increases with increasing bulkiness of substituents.

Effects of Temperature and Oxygen on Degradation. With polymers that were somewhat or very stable at room temperature, the stability at higher temperatures was studied. Figure 1 shows the molecular weight dis-

Table I
Polymerization of Substituted Acetylenes

monomer	catalyst	polymn condn[a]	polym yield, %	$\bar{M}_n/10^3$ ($\bar{M}_w/\bar{M}_n$)[b]	ref
$HC{\equiv}C\text{-}n\text{-}C_4H_9$	$Fe(acac)_3\text{-}Et_3Al$ (1:3)	A	81	82 (5.0)	13
$HC{\equiv}CCH(CH_3)_2$	$Fe(acac)_3\text{-}Et_3Al$ (1:3)	A	86	470 (2.2)[c]	14
$HC{\equiv}CC(CH_3)_3$	$MoCl_5$	B	82	93 (2.3)[d]	15
$HC{\equiv}CPh$	$W(CO)_6\text{-}CCl_4\text{-}h\nu$	C	60	60 (3.3)	16
$CH_3C{\equiv}C\text{-}n\text{-}C_3H_7$	$MoCl_5\text{-}Ph_4Sn$ (1:1)	A	87	85 (3.3)	17
$CH_3C{\equiv}C\text{-}n\text{-}C_5H_{11}$	$MoCl_5\text{-}Ph_4Sn$ (1:1)	D	88	120 (2.2)	17
$CH_3C{\equiv}C\text{-}n\text{-}C_7H_{15}$	$MoCl_5\text{-}Ph_4Sn$ (1:1)	D	55	170 (2.6)	17
$CH_3C{\equiv}CPh$	$TaCl_5$	E	70	84 (2.7)	18
$C_2H_5C{\equiv}CPh$	$NbCl_5$	F	89	74 (3.7)	18
$n\text{-}C_6H_{13}C{\equiv}CPh$	$NbCl_5$	F	57	140 (2.9)	18
$ClC{\equiv}CPh$	$Mo(CO)_6\text{-}CCl_4\text{-}h\nu$	C	52	220 (3.6)	19
$CH_3C{\equiv}CSi(CH_3)_3$	$TaCl_5$	F	90	460 (3.0)	20
$CH_3C{\equiv}CSi(CH_3)_2\text{-}n\text{-}C_6H_{13}$	$TaCl_5\text{-}Ph_3Bi$ (1:1)	F	70	470 (2.1)	21

[a] (A) Polymerized in toluene at 30 °C for 24 h, $[M]_0$ = 1.0 M, [Cat] = 20 mM. Part of the polymerization conditions were changed as follows: (B) for 1 h; (C) in CCl_4, [Cat] = 10 mM; (D) $[M]_0$ = 0.50 M, [Cat] = 30 mM; (E) at 80 °C for 6 h; (F) at 80 °C. [b] Determined by GPC on the basis of a polystyrene calibration. [c] Cis content 72%. [d] Cis content 76%.

Table II
Stability of Polyacetylenes in Air at Room Temperature in the Dark[a]

$-(CR_1{=}CR_2)_n-$		$\bar{M}_n/10^3$ ($\bar{M}_w/\bar{M}_n$)[b]			
R_1	R_2	starting polym	polym after 3 months[a]	C=O, OH in IR spectrum[c]	stab. at room temp
H	$n\text{-}C_4H_9$	82 (5.0)	1.9 (2.1)	strong	highly unstable
H	$CH(CH_3)_2$	470 (2.2)	1.4 (1.5)		
H	Ph	60 (3.3)	23 (9.8)	weak	moderately stable
CH_3	$n\text{-}C_3H_7$	85 (3.3)	70 (3.3)		
CH_3	$n\text{-}C_5H_{11}$	120 (2.2)	100 (2.5)		
CH_3	$n\text{-}C_7H_{15}$	170 (2.6)	100 (3.1)		
H	$C(CH_3)_3$	no change in $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$		no	highly stable
CH_3	$Si(CH_3)_3$				
CH_3	$Si(CH_3)_2\text{-}n\text{-}C_6H_{13}$				
CH_3	Ph				
C_2H_5	Ph				
$n\text{-}C_6H_{13}$	Ph				
Cl	Ph				

[a] Polymers were left in air at room temperature for 3 months in the dark. [b] Determined by GPC on the basis of a polystyrene calibration. [c] IR spectra of polymers after 3 months; C=O, 1720, 1750 cm^{-1}; OH, 3425 cm^{-1}.

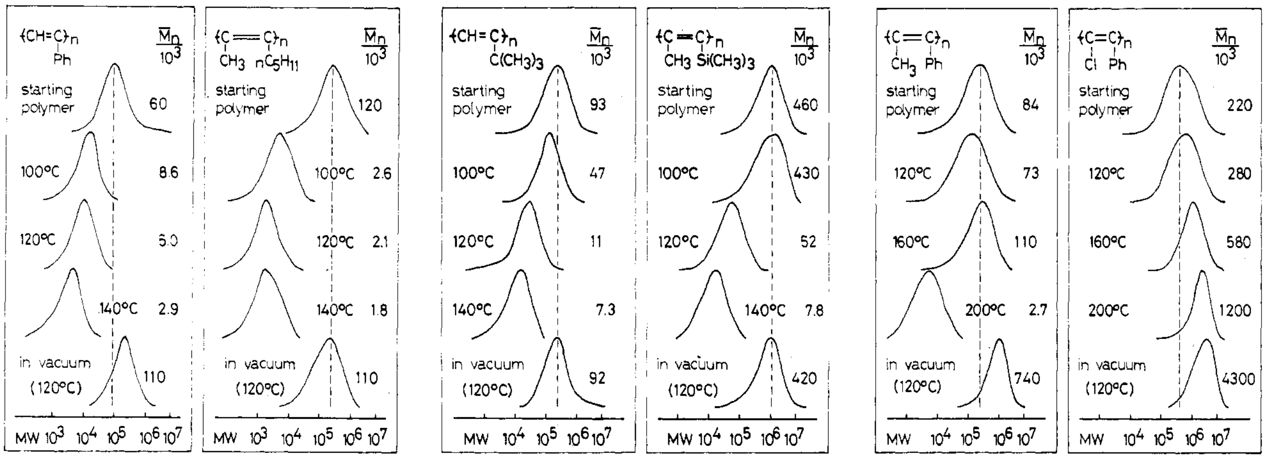


Figure 1. MWD changes with the heat treatment of polyacetylenes carrying substituents (powdery polymers were heated for 20 h in the presence or absence of air).

tribution (MWD) of the polymers (GPC curves) before and after heat treatment in air at 100–200 °C for 20 h.

As seen in Figure 1, poly(phenylacetylene) and poly(2-octyne) markedly degraded at 100 °C or above, resulting in oligomers ($\bar{M}_n$ = 2000–3000). Poly(*tert*-butylacetylene) and poly[1-(trimethylsilyl)-1-propyne] were fairly stable around 100 °C, with no large molecular weight change observed. Their molecular weights, however, appreciably decreased when they were heat-treated above 120 °C. The shapes of the MWD curves before and after the heat treatments hardly changed for any of the polymers, which suggests that degradation takes place at random.

Poly(1-phenyl-1-propyne) and poly(1-chloro-2-phenylacetylene) proved even more stable. Poly(1-phenyl-1-propyne) was stable below 160 °C, though it degraded at 200 °C. The molecular weight of poly(1-chloro-2-phenylacetylene) did not decrease even at 200 °C but tended to increase. This seems to be due to cross-linking, though the polymer remained soluble.

Very interestingly, no decrease in molecular weight was observed under vacuum with any of these polymers, including poly(2-octyne), which underwent remarkable

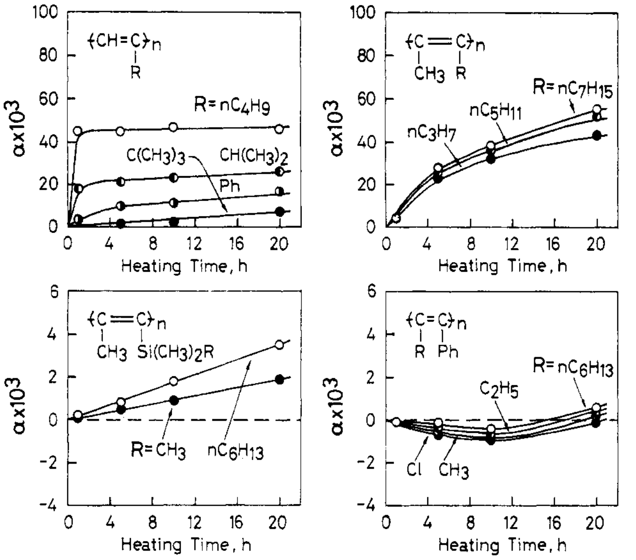


Figure 2. Relationship between the period of heating time and the probability of main-chain bond scission (α) for polyacetylenes carrying substituents (powdery polymers were heated in air at 120 °C).

degradation in air. This finding shows that oxygen in air is necessary for polymer degradation to occur.

Polymer Structure and Degradability. To estimate the degradability of each polymer, we discuss a probability that the main-chain bonds undergo scission when a polymer is heat-treated at a temperature for a given time. This probability will be referred to as the "α value" and is defined by the equation

$$\alpha \equiv \frac{S}{\overline{\mathrm{DP}}_{\mathrm{n},0} - 1} = \frac{\overline{\mathrm{DP}}_{\mathrm{n},0} - \overline{\mathrm{DP}}_{\mathrm{n}}}{\overline{\mathrm{DP}}_{\mathrm{n}}(\overline{\mathrm{DP}}_{\mathrm{n},0} - 1)} \simeq \frac{1}{\overline{\mathrm{DP}}_{\mathrm{n}}} - \frac{1}{\overline{\mathrm{DP}}_{\mathrm{n},0}} \qquad \left(S \equiv \frac{\overline{\mathrm{DP}}_{\mathrm{n},0}}{\overline{\mathrm{DP}}_{\mathrm{n}}} - 1 \right)$$

where S is the times that main-chain scission occurs in one molecule of a polymer and $\overline{\mathrm{DP}}_{\mathrm{n},0}$ and $\overline{\mathrm{DP}}_{\mathrm{n}}$ are respectively the initial and final number-average degrees of polymerization for the polymer.

Use of the α value enables direct comparison of the degradabilities of polymers having different molecular weights. For instance, if the α value of a polymer under a certain condition is 0.01, it means that every hundredth bond cleaves irrespective of the original molecular weight of the polymer. A negative value of α indicates occurrence of cross-linking, though its physical meaning is not simply expressed. Figure 2 shows the plots of α values as a function of time in the heat treatment of polymers in air at 120 °C.

In the case of polymers from aliphatic monosubstituted acetylenes, polymer degradability decreased with increasing bulkiness of substituents: Poly(1-hexyne) and poly(isopropylacetylene) degraded quickly to oligomers having molecular weights of a few thousand, and accordingly their α values sharply increased. On the other hand, the α value of poly(*tert*-butylacetylene) was much smaller under the same conditions.

Though degradation rates of poly(2-alkynes) are lower than those of poly(1-hexyne) and poly(isopropylacetylene), their α values increased considerably as time elapsed. In comparison with poly(2-alkynes), the two Si-containing polymers shown in Figure 2 have α values only $^1/_{10}$ as large, which proves that they are fairly stable polymers.

The α values of polymers from aromatic disubstituted acetylenes are at first small and negative but change later to small and positive values. Anyhow, these values are very small, thus meaning that these polymers are highly stable.

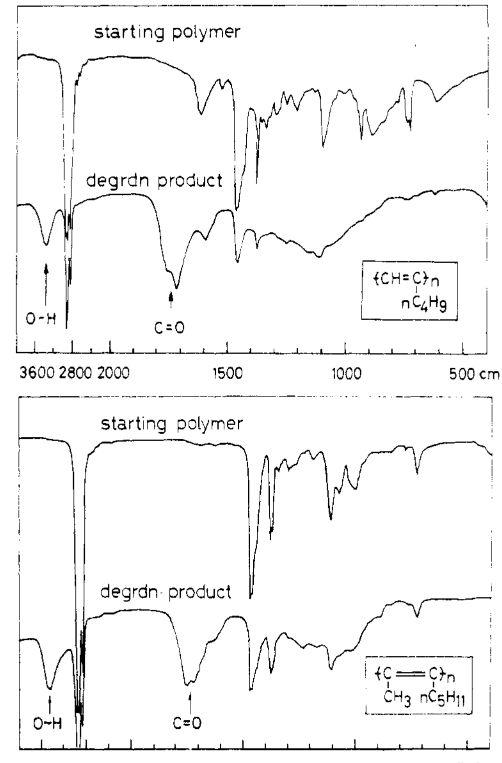


Figure 3. IR spectra of starting polymers and thermal-degradation products (heat treatment in air at 120 °C for 20 h).

The above results lead to the following order of thermal stability: $-[\mathrm{CH{=}C}(n\text{-Bu})]_n-$, $-[\mathrm{CH{=}C}(i\text{-Pr})]_n-$ < $-[\mathrm{CH{=}CPh}]_n-$, $-[\mathrm{CMe{=}CR}]_n-$ < $-[\mathrm{CH{=}C}(t\text{-Bu})]_n-$, $-[\mathrm{CMe{=}C(SiMe_2R)}]_n-$ < $-[\mathrm{CR{=}CPh}]_n-$, $-[\mathrm{CCl{=}CPh}]_n-$. Here, R stands for n-alkyl groups.

Degradation Products. As has been described above, the presence of oxygen is essential to the present polymer degradation. Hence, the oxidation process and degradation products were investigated. The degradation product of poly(2-octyne) was studied in particular detail because it was moderately stable at room temperature and easily degradable at high temperature.

The IR spectra of the degradation products of poly(1-hexyne) and poly(2-octyne) clearly show absorption bands due to C=O (1800–1700 cm^{-1}) and OH groups (~3400 cm^{-1}) (Figure 3). This indicates that during thermal degradation these polyacetylenes reacted with an oxygen molecule to form oxygen-containing compounds. On the other hand, polymers of aromatic disubstituted acetylenes were not degraded by heat treatment in air at 120 °C for 20 h, and accordingly neither C=O nor OH bond was observed in the IR spectra after the heat treatment. These results imply that the present degradation must be accompanied by the oxidation process.

According to elemental analysis, the degradation product of poly(2-octyne) in air at 120 °C for 20 h contained much oxygen, up to about 0.8 atom per repeating unit (Table III). When this high oxygen content is compared with the corresponding α value (e.g., the content of oxygen atom is ca. 15 times as high as the probability of chain scission (α) at a heating time of 20 h), it turns out that only part of the oxidized moieties participate in the main-chain scission.

In accordance with the uptake of much oxygen in the form of C=O and OH groups, the degradation product of poly(2-octyne) exhibited a different solubility property

Table III
Thermal-Oxidation Product of Poly(2-octyne)[a]

heating time, h	O_2 content,[b] wt %	O atoms per repeat unit[c]	α[d]	solubility in 2-butanone[e]	% wt change[f]
0	0	0	0	I	0
1	1.7	0.12	0.004	I	+0.3
5	6.6	0.46	0.026	Sw	+0.7
10	11.4	0.79	0.036	S	+0.9
20	10.9	0.75	0.052	S	−0.3

[a] Heated in air at 120 °C. [b] By elemental analysis. [c] Calculated from the oxygen content of oxidation product. [d] Probabilities of the main-chain bond scission during given times. [e] I, insoluble; Sw, swollen; S, soluble. [f] Determined by isothermal gravimetric measurement of TGA.

from that of the starting polymer. For example, the product dissolved in polar solvents like 2-butanone and ethyl acetate, which are nonsolvents of poly(2-octyne).

The isothermal gravimetric analysis of poly(2-octyne) was carried out in air at 120 °C (see Table III). Consequently it proved that the weight change of poly(2-octyne) during heat treatment remained less than 1%. When the uptake of oxygen from air is considered, poly(2-octyne) is presumed to have lost about 10% of its weight as volatile materials. Thus, although both main-chain scission and side-chain scission can occur, the former eventually causes the remarkable molecular weight decrease while the latter produces no significant effect at a relatively low temperature like 120 °C.

Thermogravimetric Analysis. Practically no weight change was observed during the heat treatment of any polymers of *tert*-butylacetylene and disubstituted acetylenes in air at 120 °C. It is interesting to observe the temperature of the initial weight loss of these polymers and how substituents in the polymers affect the stability. Figure 4 illustrates TGA curves of various polyacetylenes measured in a range from room temperature to 500 °C.

The weight loss of poly(1-hexyne) and poly(isopropylacetylene) starts at temperatures as low as 150 °C. Poly(*tert*-butylacetylene) and poly(phenylacetylene) retain their weight up to ca. 200 °C, thus being more stable. In any case, an air or nitrogen atmosphere does not appear to have a substantial influence on the stability.

Poly(2-octyne) and poly(2-decyne), which are polymers of aliphatic disubstituted acetylenes, begin to lose weight at ca. 200 °C in air and at ca. 300 °C in a nitrogen atmosphere. Though the reason is not clear, the presence or absence of oxygen affects greatly the stability of these polymers.

Polymers of aromatic disubstituted acetylenes maintain their weight up to ca. 300 °C even in air. In this way, these polymers are the most stable among the various polyacetylenes also with respect to weight retention.

The starting temperature of weight loss of poly[1-(trimethylsilyl)-1-propyne][20] and poly[1-(dimethyl-*n*-hexylsilyl)-1-propyne][21] in air is ca. 250 °C; thus these polymers are fairly stable.

The molecular weight decrease of a polymer is caused effectively by random main-chain scission. On the other hand, weight loss of the polymer stems from the formation of volatile materials by all types of chain scission. However, it is interesting to note that the facility of the molecular weight decrease of a polymer in the present study corresponds to the ease of the weight loss of the polymer.

Discussion

Features of the Thermal Degradation. Features of the thermal degradation of polyacetylenes with substituents include the following:

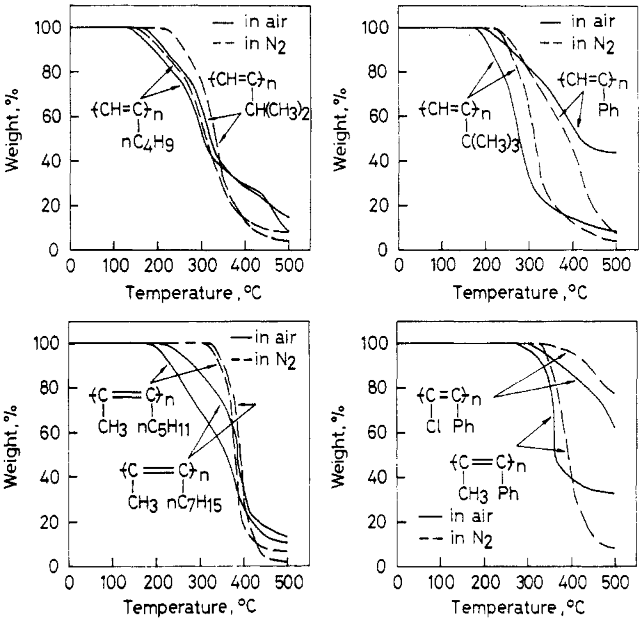


Figure 4. TGA curves of polyacetylenes carrying substituents (heating rate 10 °C/min).

(i) None of polymers from *tert*-butylacetylene, 1-(trimethylsilyl)-1-propyne, and aromatic disubstituted acetylenes undergo oxidation or molecular weight decrease when they are left in air at room temperature for a long period of time. This presents a striking contrast with the notorious instability of polyacetylene and is of great importance on application of these polymers to practical uses.

(ii) Polymer stability increases with increasing number and/or bulkiness of substituents. This can be explained as follows. When the number and/or bulkiness of substituents increases, then, owing to the steric effect of substituents (a) the main chain takes a more twisted conformation so that the polymers can hardly produce biradicals and/or (b) double bonds of the main chain are more protected from attack by oxygen.

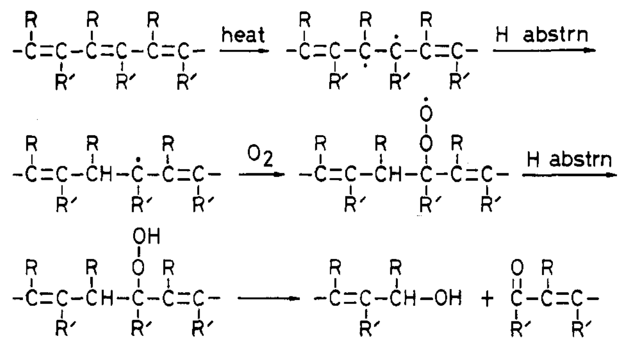
(iii) None of the present polymers suffer degradation under vacuum. This indicates that the oxidation process must precede the molecular weight decrease of polymers. This result contrasts with the fact that degradation of vinyl polymers such as methyl methacrylate and α-methylstyrene does not require oxygen.[22]

The behavior of the present thermal degradation resembles in many aspects that of γ-ray radiolysis of the same polymers,[12] e.g., influence of polymer structure, necessity of air, and degradation products.

Degradation Mechanism. Several possible processes have been proposed for the oxidation of polyacetylene[3] and polypropyne,[5] which are also suggestive for the present thermal degradation of various polyacetylenes with substituents. On the basis of the above-stated results and by analogy with γ-ray radiolysis of these polymers,[12] we infer that the present degradation involves the following elementary steps in its principal process: (i) thermal formation of biradicals; (ii) conversion of biradicals to monoradicals via hydrogen abstraction; (iii) formation of hydroperoxides by reaction of polymer radicals with oxygen molecules; (iv) bond scission on the main chain and formation of C═O and OH groups.

Scheme I depicts one of the most probable degradation processes including the above elementary steps. The presence of step ii will be demonstrated by the following observations in electron spin resonance (ESR):[23] (a) no triplet-state radicals are found; (b) the polymer radicals formed under vacuum at high temperature do not decrease

Scheme I



even if temperature is lowered (biradicals would revert to π-bonds).

The especially high stability of polymers of aromatic disubstituted acetylenes seems to be due to the following reasons: (a) it is difficult for these polymers to form biradicals because their main chain is highly twisted;[18] (b) the abstraction of hydrogen from phenyl group is impossible, which makes the monoradical formation less facile; (c) the presence of phenyl and another group protects radicals on the main chain from the attack by oxygen. Since the opposite effects are expected for polymers of linear monoalkylacetylenes, they should be unstable; this agrees with the present result.

The study of degradation intermediates by ESR and spin trapping is now under way.

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Registry No. $(HC\equiv CC_4H_9\text{-}n)_n$ (homopolymer), 28827-85-2; $(HC\equiv CCH(CH_3)_2)_n$ (homopolymer), 87926-66-7; $(HC\equiv CPh)_n$ (homopolymer), 25038-69-1; $(CH_3C\equiv CC_3H_7\text{-}n)_n$ (homopolymer), 42121-00-6; $(CH_3C\equiv CC_5H_{11}\text{-}n)_n$ (homopolymer), 80652-33-1; $(CH_3C\equiv CC_7H_{15}\text{-}n)_n$ (homopolymer), 80652-35-3; $(HC\equiv CC(CH_3)_3)_n$ (homopolymer), 51730-68-8; $(CH_3C\equiv CSi(CH_3)_3)_n$ (homopolymer), 87842-32-8; $(CH_3C\equiv CSi(CH_3)_2\text{-}n\text{-}C_6H_{13})_n$ (homopolymer), 93094-72-5; $(CH_3C\equiv CPh)_n$ (homopolymer), 53621-07-1; $(C_2H_5C\equiv CPh)_n$ (homopolymer), 94844-29-8; $(n\text{-}C_6H_{13}C\equiv CPh)_n$ (homopolymer), 98705-03-4; $(ClC\equiv CPh)_n$ (homopolymer), 81953-16-4.

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