Autoxidation and Stabilization of Poly(methylacetylene)

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ABSTRACT: Thermal oxidation and photooxidation of poly(methylacetylene) have been studied between 40 and 70 °C on polymer films by oxygen uptake and infrared absorption of the carbonyl and hydroxyl products. The rate of thermal oxidation at 70 °C is 10^{-6} mol g^{-1} s^{-1} with an apparent activation energy of 14.6 kcal mol^{-1}. The rate is linearly dependent upon oxygen pressure, indicating its participation in the initiation process. Various types of stabilizers were investigated for their efficiency. Singlet-oxygen quenchers such as 9,10-dimethylanthracene are ineffective. Radical scavengers of the hindered phenol type inhibit thermal oxidation for a time and retard the subsequent oxidation. Hydroperoxide decomposers by themselves have no effect but show synergism when used together with a radical scavenger. The presence of a spin trap, *N-tert*-butyl-2-phenylnitrone, yielded a nitroxide EPR signal. The spin trap alone has no effect on the autoxidation of poly(methylacetylene). However, when it is used with 2,6-di-*tert*-butyl-*p*-cresol the induction period is doubled and the subsequent rate of oxidation halved. The results suggest that carbon radicals, oxy radicals, and hydroperoxides are intermediates in the free radical chain autoxidation processes. The photooxidation of poly(methylacetylene) is only weakly retarded by some stabilizers, the most effective being the hindered amine type. The oxidized polymer is soluble in methyl ethyl ketone and other solvents and unchanged in molecular weight or distribution; therefore, there is no significant cross-linking occurring during oxidation.

Polyacetylene, which becomes highly conducting upon doping, has been the subject of intense research efforts. By its chemical nature, polyacetylene displays marked thermal, chemical, and environmental sensitivities, which tend to limit its scope of applications. In particular, polyacetylene interacts with oxygen in a variety of ways. Brief exposure of *trans*-polyacetylene to air increases its EPR line width from ca. 0.5 to 2.5 G with no net change in spin concentration.[1] Evacuation returns the EPR spectrum to the original, and so this effect is apparently reversible. On the other hand, Holczer et al.[2] found that long exposure of this polymer to air decreases the proton spin–lattice relaxation time irreversibly. The results of dynamic nuclear polarization on *trans*-polyacetylene after exposure to air show a mixture of electron Overhauser and solid-state effects, whereas only the former effect is seen for polymer samples not exposed to air. Pristine *cis*-polyacetylene never exposed to air or kept at −78 °C is devoid of an EPR signal but develops a $g = 2$ resonance upon admission of oxygen.[3] This indicates the development of neutral defects[4] and cis–trans isomerization. In fact, oxygen has been used to catalyze this isomerization, significantly lowering the activation energy for the uncatalyzed process.[5] Oxygen also strongly affects the electrical conductivity of polyacetylene in a complicated fashion.[6,7] Exposure of *cis*-polyacetylene to oxygen greatly reduces its tensile strength, ductility, and extensibility.[8,9] With this multitude of modes of interaction between oxygen and polyacetylene, it would be difficult to study the autoxidation and stabilization of the polymer. There is the additional severe physical limitation of insolubility and crystallinity.

Poly(methylacetylene) resembles polyacetylene in many respects but differs in others. Poly(methylacetylene) is soluble in organic solvents,[10] is a wide band-gap insulator, and is devoid of delocalized free spins. It cannot be doped by AsF_5 but interacts reversibly with iodine to attain a low conductivity of 10^{-5} $(\Omega\ cm)^{-1}$. However, copolymers of acetylene and methylacetylene have properties intermediate between those of the homopolymers. Because of the solubility of poly(methylacetylene) it offers a good model for the study of autoxidation and stabilization of a polymer with a conjugated backbone.

The central purpose of this work is to investigate the kinetics and mechanisms of autoxidation of poly(methylacetylene) and the effect of antioxidants, with obvious extension to similar studies on polyacetylene.

Experimental Section

Materials. Methylacetylene from Matheson was condensed into a Schlenk tube containing P_2O_5 at −78 °C for 20–30 min, transferred into a cold finger maintained at −196 °C, pumped to remove traces of N_2 or O_2, and stored until use.

Titanium tetrabutoxide (Alfa Inorganics) was purified by reduced-pressure distillation under a slow argon bleed. The center cut of the distillate was collected and stored under argon in a Schlenk tube wrapped with black tape.

Toluene (Fisher) was twice treated with concentrated H_2SO_4 overnight and then washed twice with distilled water, thrice with 10% NaOH, and repeatedly with deionized water until neutral to litmus. It was dried over anhydrous $MgSO_4$, filtered, refluxed over CaH_2, treated with triethylaluminum, and distilled freshly before use. Tetrachloroethylene (Eastman Organics) was degassed several times and stored under nitrogen.

The stabilizers used in this work and their sources are as follows: phenylenediamine, hydroquinone, 9,10-dimethylanthracene (DMA), 2,6-di-*tert*-butyl-*p*-cresol (BHT), *N*-phenyl-*N′*-cyclohexylphenylenediamine (4010), and *N-tert*-butyl-2-phenylnitrone (BPN) were from Aldrich; tris(*p*-nonylphenyl) phosphite (TNP) and distearyl thiodipropionate (DSTDP) were gifts from Borg-Warner Chemicals; bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (Tinuvin 770) and methanetetrayltetrakis(methyl (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)) (Irganox 1010) were gifts from Ciba-Geigy. They were used as received. The stabilizers were incorporated by codissolving the stabilizers with poly(methylacetylene) in either toluene or methylene chloride and evaporating to dryness under nitrogen to form the stabilized polymer films.

Polymerization of Methylacetylene. The catalyst was prepared as described previously[10] in a Schlenk tube by mixing 1.7 mL of Ti(O-*n*-Bu)$_4$ with 2.7 mL of $AlEt_3$ in 20 mL of toluene and aged 15 min at room temperature. The solution was cooled to −78 °C and thoroughly degassed. It was warmed to 0 °C and the monomer introduced from a 2-L storage bulb. Polymerization proceeded with vigorous stirring for 90–120 min, consuming ca. 560 torr of methylacetylene. The polymer was precipitated with methanolic HCl, purified by repeated filtration, dissolution in toluene, reprecipitation, and finally washed several times with oxygen-free anhydrous methanol. Vacuum drying yielded 1.1 g of poly(methylacetylene). Anal.: C, 89.06; H, 9.7. The polymer has a molecular weight of 1500–9000, depending upon polymerization conditions. Films (ca. 0.4 mil thick) were cast from a

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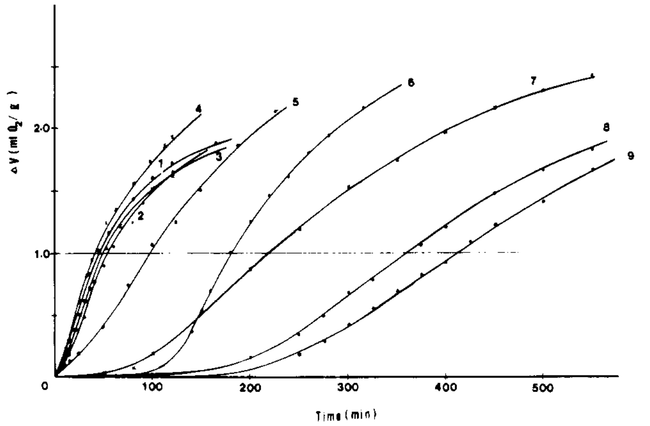


Figure 1. Oxygen uptake curves for poly(methylacetylene) films at 70 °C and 760 torr of O_2: (1) without additive; (2) 1% TNP; (3) 1% DSTDP; (4) 1% DMA; (5) 1% Tinuvin 770; (6) 1% 4010; (7) 1% BHT; (8) 1% BHT + 1% TNP; (9) 1% BHT + 1% DSTDP.

tetrachloroethylene solution of the polymer under purified nitrogen.

Infrared Spectra. A Perkin-Elmer 283 grating spectrophotometer was used to obtain IR spectra. Poly(methylacetylene) film was cast from an appropriate solution directly onto a NaCl plate and dried under nitrogen. The thickness of the polymer film is about 0.4 mil. Autoxidation was carried out under a controlled atmosphere of oxygen and temperature. The specimens were periodically monitored for spectral changes. For photooxidation, samples were irradiated with a 450-W medium-pressure mercury lamp under 1 atm of oxygen and their spectra periodically recorded.

Oxygen Uptake. Films of poly(methylacetylene) of about 30 mg were coated on glass slides and placed in an automatic oxygen uptake apparatus.[11-14] The assembly was evacuated for 5 min, immersed in a thermostated paraffin oil bath at the required temperature under vacuum for another 5 min, and then filled with pure oxygen to 760 torr. The consumption of oxygen under a constant pressure was monitored as soon as thermal equilibrium was established. Measurements were usually made at 760 torr of oxygen, but some were made at 1 atm of air as well.

Molecular Weights. The molecular weight and distribution of poly(methylacetylene) were determined with a Waters Associates GPC apparatus.

Electron Paramagnetic Resonance. A Varian E-9 X-band spectrometer was used in the EPR studies.

Results

Autoxidation of Poly(methylacetylene). The autoxidation of poly(methylacetylene) as measured by oxygen uptake is shown in curve 1 of Figure 1. Though it bears a superficial resemblance to the autoxidation of other polymers such as polyolefin,[11-14] there are distinct differences. There was virtually no induction period; oxygen consumption begins immediately though at a slightly slower rate, which may be due to thermal equilibration. The maximum rate of oxidation at 70 °C is about 9.9×10^{-7} mol g^{-1} s^{-1}. The oxidation curve for polyacetylene is almost identical with that of poly(methyacetylene).[15] For both polymers, there is no extended period during which the rate of oxidation remains constant as there is in the autoxidation of polyolefins. The oxidation curve is hyperbolic in shape in the absence of an effective inhibitor. In contrast, the rate of autoxidation of polyolefins remained constant for an extended period and then became very slow upon nearing completion. Typically for polyolefins the maximum uptake of oxygen is ca. 10 mL per gram of polymer under these conditions. The oxygen uptake is far greater for poly(methylacetylene) (and also for polyacetylene); curve 1 of Figure 1 showed that 100 mL of oxygen was taken up by the polymer, corresponding to 0.18 mol of O_2 per mole of monomer unit. The polymer is probably capable of consuming even more oxygen if the experiment were allowed to continue.

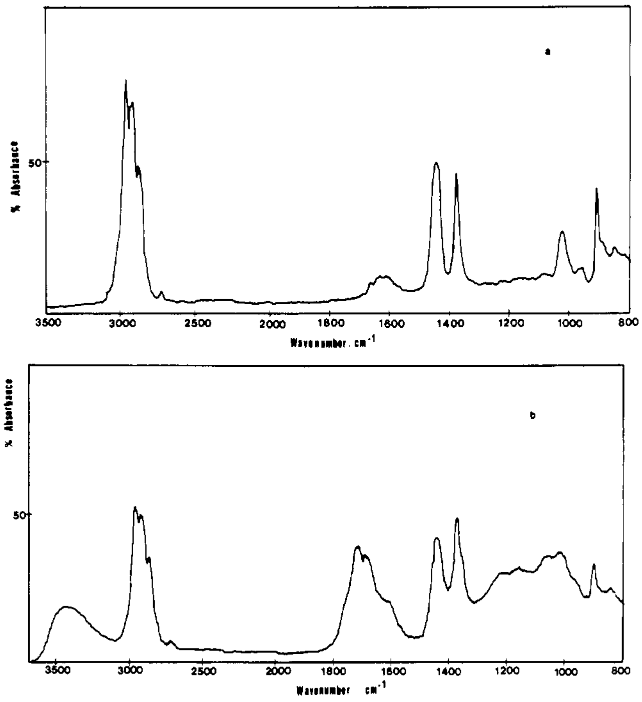


Figure 2. Infrared spectra: (a) freshly prepared poly(methylacetylene) containing 1% BHT; (b) polymer free of stabilizer exposed to O_2 at 60 °C for 880 min.

Another way to monitor the autoxidation is through infrared spectroscopy. Figure 2a shows a spectrum of pristine poly(methylacetylene);[10] the spectrum after 14.7-h exposure to O_2 at 60 °C is shown in Figure 2b. The spectra were obtained on film cast from a concentrated solution of the polymer. The two bands at 1375 and 1460 cm^{-1} are assigned to the methyl group symmetric and antisymmetric bending vibrations, respectively. The other bands in the order of increasing frequencies are tentatively assigned to 910 cm^{-1} (=CH rocking mode), 1620 cm^{-1} (C=C), and 2960, 2920, and 2875 cm^{-1} (CH_3 stretching vibrations).

As poly(methylacetylene) oxidizes, the following spectral changes were observed. There is produced a broad band with ν_{max} at 3420 cm^{-1} of about 300-cm^{-1} width, which may be attributed to the OH stretching vibration of a hydroperoxyl or hydroxyl group hydrogen bonded to a carbonyl group or another hydroperoxyl and hydroxyl groups.[14] In the carbonyl region the ν_{max} at 1720 and 1680 cm^{-1} are probably the bands for carbonyl and C=C—C=O groups. The CH_3 stretching modes decrease in intensity with oxidation, as expected. There is an absorption intensity increase beneath the prominent 1375- and 1460-cm^{-1} bands, which is believed to be related to the bending vibration of methylene groups (connected to OH). Finally, there is increasing absorption in the 1000–1300-cm^{-1} region, which could be associated with vibrations of peroxy groups. Several of the above bands have been observed and similarly assigned in oxidized polyacetylene.[15,16]

It was observed that the total area between 1300 cm and 1500 cm^{-1} remains constant as methyl groups are oxidized to methylene groups. Apparently, any decrease in the absorbances of the former is compensated by the latter. Therefore, it is possible to monitor the rate of autoxidation from the increase of the OH band at 3420 cm^{-1} or of the carbonyl band at 1720 cm^{-1} with respect to the absorbance between 1300 and 1500 cm^{-1}. Figure 3 gives the variation of $A(>C{=}O)/A(CH_3 + {=}CH_2)$ and $A(OH)/A(CH_3 +$

Table I
Comparison of Autoxidation of Poly(methylacetylene) at 70 °C in Air and Oxygen

	time, min to $\left(\frac{A(>C=O)}{A(CH_3 + =CH_2)}\right) = 1.0$	initial slope		final slope	
		$>C=O$ band	OH band	$>C=O$ band	OH band
air	182	0.009	0.005	0.0008	0.0002
oxygen	37	0.028	0.023	0.002	0.0009
ratio (air/O_2)	4.9	0.32	0.21	0.4	0.22

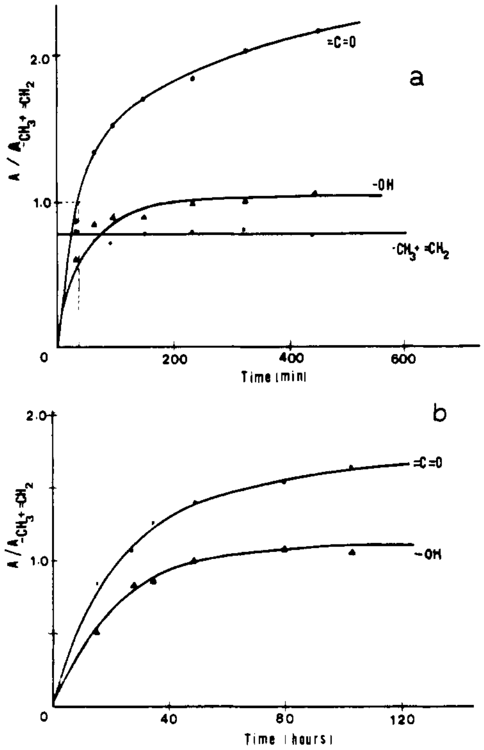


Figure 3. Variation of $A(>C=O)/A(CH_3 + =CH_2)$ and $A(OH)/A(CH_3 + =CH_2)$ with time of oxidation: (a) 70 °C, (b) 25 °C; 760 torr of O_2.

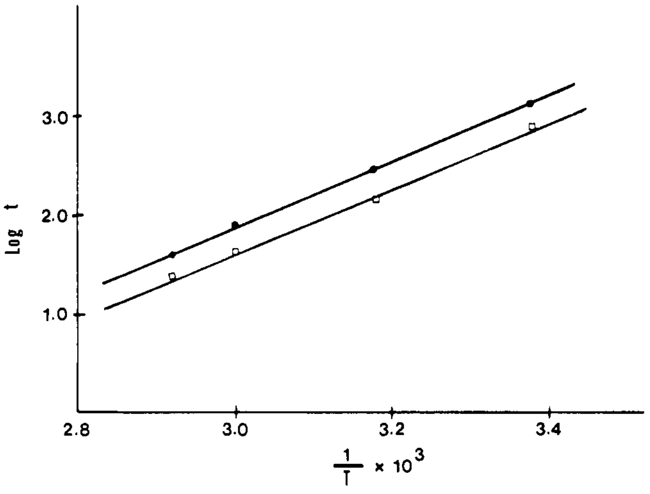


Figure 4. Arrhenius plot for autoxidation of poly(methylacetylene): (●) for C=O formation; (□) for OH formation.

$=CH_2$); the time it takes to reach a ratio of 1.0 and 0.6, respectively, was used to obtain the Arrhenius plot (Figure 4). From the results obtained between 22 and 70 °C, the apparent activation energy of autoxidation was found to be 14.6 kcal mol^{-1}.

Oxidation of poly(methylacetylene) results in a decrease of conjugation length. This is shown by the electronic spectra (Figure 5); after 60 h of exposure to air at 22 °C, the absorption is blue shifted by ca. 30 nm.

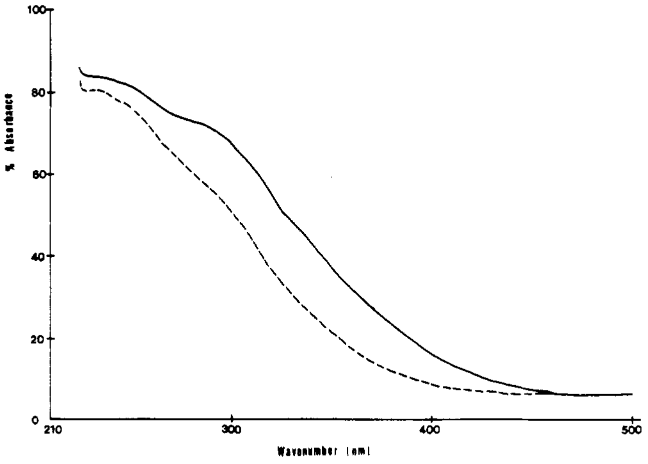


Figure 5. Electronic spectra of poly(methylacetylene): (—) before oxidation; (- - -) after exposure to air for 60 h at 25 °C. 2.5 mg of polymer in 100 mL of CH_2Cl_2.

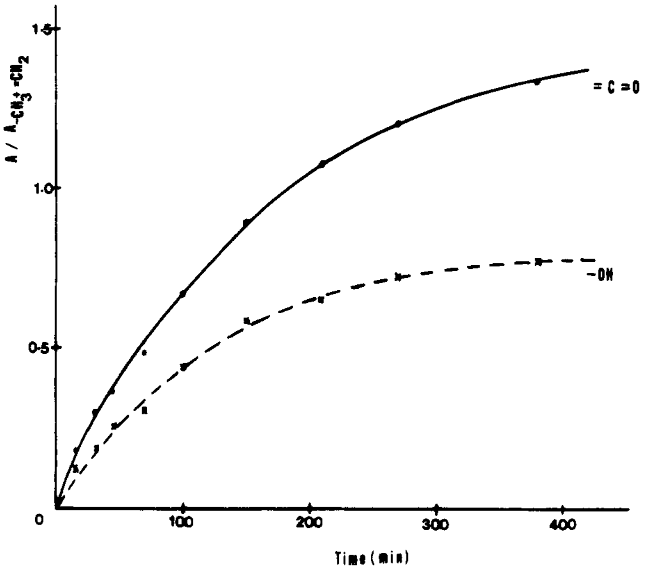


Figure 6. Autoxidation of poly(methylacetylene) in an atmosphere of air at 70 °C.

Autoxidation of poly(methylacetylene) was also performed in air (Figure 6). Table I compares these results with that obtained in pure oxygen (curve 1, Figure 1). The time to reach certain levels of oxidation (column 2) is 4.9 times longer in air than in O_2; the slope for oxygen uptake in air, both initial and final, is about 0.21 of that in O_2. These results indicate that autoxidation of poly(methylacetylene) is linearly dependent on the oxygen partial pressure. The slopes from the >C=O band differ by less than the expected ratio because the band is not completely resolved, but the slope for the formation of OH shows the expected dependence on oxygen pressure.

Inhibited Autoxidation of Poly(methylacetylene). Autoxidation of poly(methylacetylene) probably involves the actions of R·, RO·, and RO_2· radicals and hydroperoxides as in the case of polyolefins. In addition, because of the double bonds, the allylic methyl groups, and un-

Table II
Effect of Stabilizers on the Autoxidation of Poly(methylacetylene) of O_2 Uptake[a]

stabilizer	t_{ind}, min	max rate of oxidation × 10^7 mol g^{-1} s^{-1}
none	none	9.9
TNP	none	9.9
DSTDP	none	9.9
DMA	none	11.0
phenylenediamine	none	17.0
hydroquinone	23	7.9
Tinuvin 770	9	11.9
4010	117	5.9
BHT	75	2.5
BHT + TNP	175	2.1
BHT + DSTDP	225	1.9

[a] At 70 °C, 760 torr of oxygen, with 1 wt % of stabilizer.

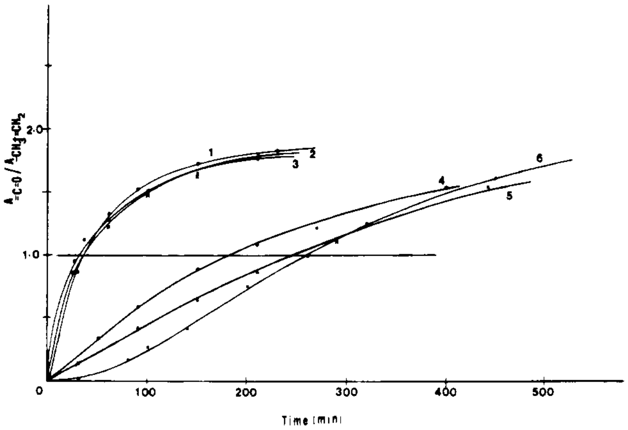


Figure 7. Effect of stabilizer on the rate of formation of carbonyl oxidation products by IR at 70 °C and 760 torr of oxygen: (1) no additive; (2) 1% DSTDP; (3) 1% DMA; (4) 1% Irganox 1010; (5) 1% BHT; (6) 1% BHT + 1% DSTDP.

paired spins in poly(methylacetylene), it is possible that singlet oxygen may participate in its oxidation. Those stabilizers that function primarily as hydroperoxide decomposers are TNP, DSTDP, and possibly hydroquinone, phenylenediamine, and 4010. The latter three may also scavenge RO· and RO_2· radicals. DMA is a singlet-oxygen quencher and Tinuvin 770 is a UV stabilizer whose complicated modes of action are still to be understood. The additives that act as RO· and RO_2· scavengers are BHT and Irganox 1010.

The results of poly(methylacetylene) autoxidation in the presence of the above stabilizers and synergistic combinations[17] are shown in Figure 1, and the t_{ind} and maximum rates of oxidation summarized in Table II. Within experimental accuracy, the autoxidation is not affected by DMA. The hydroperoxide decomposers alone (TNP and DSTDP) have no effect on the oxidation. This is as expected because phosphorus–sulfur compounds are not primary antioxidants and are effective only as synergists when used with a primary antioxidant such as BHT or Irganox 1010. Tinuvin 770 slightly retards the oxidation of poly(methylacetylene). The presence of radical scavengers BHT and 4010 elicited a distinct induction period. The induction period was significantly increased and the rates of subsequent autoxidation were retarded when BHT was used with a synergist such as TNP and DSTDP (Table II).

The inhibited autoxidation was also investigated by the IR technique as described above. The results are summarized in Table III and Figure 7. The results showed that the oxidative stabilities measured with the carbonyl and OH bands are in good agreement. Furthermore, the rankings in stabilization by oxygen uptake and IR are in general accord. The enhanced stability of DSTDP when added with BHT demonstrated the synergistic effect.[17] The total absence of effect of TNP is perplexing. It may be due to hydrolysis of the phosphite or ready oxidation to the corresponding phosphate. The superior performance of BHT over Irganox 1010 can be rationalized. The long lifetime attained by polypropylene stabilized by Irganox 1010 can be readily attributed to its compatibility with the substrate and its low volatility.[18] In a 150 °C circulating-air oven-aging test, BHT was volatilized in a few hours. On the other hand, for poly(methylacetylene), which oxidizes so readily, the higher diffusivity of BHT over Irganox 1010 is an advantage.

Table III
Effect of Stabilizers on the Autoxidation of Poly(methylacetylene) by IR Spectra[a]

stabilizer	time in min to reach $A(C{=}O)/A(CH_3 + {=}CH_2) = 1.0$	time in min to reach $A(OH)/A(CH_3 + {=}CH_2) = 0.6$
none	37	32
TNP	35	30
DMA	42	38
DSTDP	35	35
Irganox 1010	178	110
BHT	250	250
Irganox 1010 + DSTDP	175	115
BHT + TNP	200	190
BHT + DSTDP	260	280

[a] At 70 °C, 760 torr of oxygen, with 1 wt % of stabilizer. The carbonyl absorptions of the stabilizers, i.e., DSTDP and Irganox 1010, were too weak to be observed.

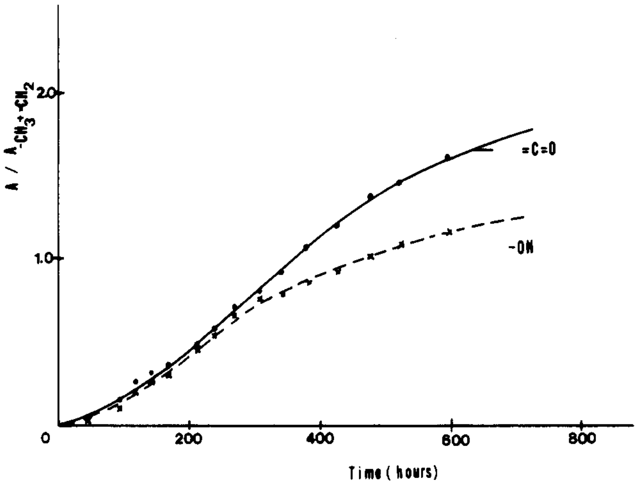


Figure 8. Autoxidation of poly(methylacetylene) stabilized by 1% BHT; P_{O_2} = 760 torr.

Figure 8 shows the autoxidation of poly(methylacetylene) containing 1% BHT at 22 °C. This and similar data at other temperatures afforded an Arrhenius plot shown in Figure 9 which gives a value of 18.9 kcal mol^{-1} for the activation energy.

Photooxidation of Poly(methylacetylene). A 450-W medium-pressure mercury lamp with water cooling was used to irradiate poly(methylacetylene) films under 760 torr of oxygen. The Pyrex glass container effectively filtered out radiation with wavelengths shorter than 280 nm. The distance separating the light source and the specimen was maintained at 8 cm. The results of photooxidation

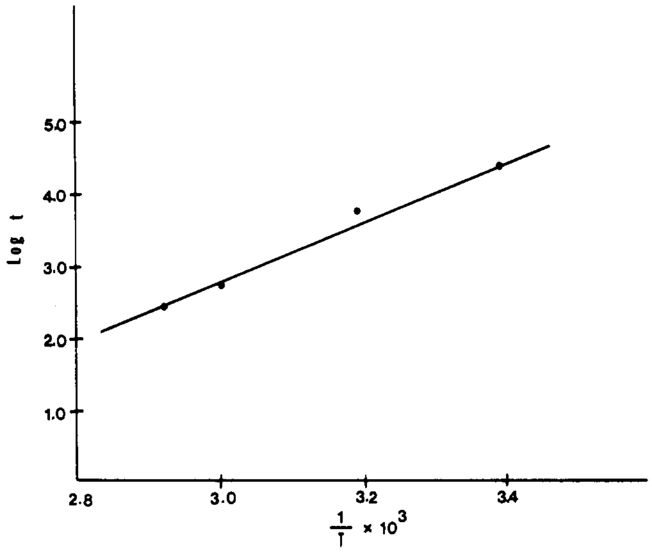


Figure 9. Arrhenius plot for autoxidation of poly(methylacetylene) stabilized by 1% BHT.

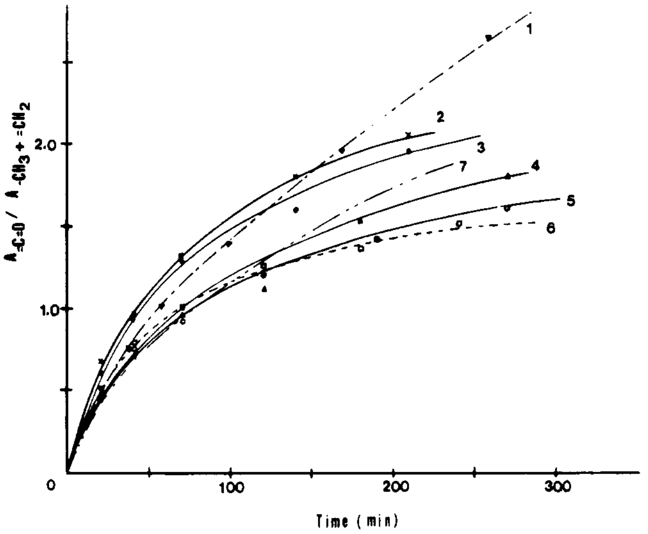


Figure 10. Photooxidation curves for poly(methylacetylene) irradiated with a medium-pressure mercury lamp for 260 min at 25 °C and 760 torr of O_2: (1) no additive; (2) 1% 4010; (3) 1% BHT; (4) 1% BHT + 1% DSTDP; (5) 1% Irganox 1010; (6) 1% Tinuvin 770; (7) 1% DMA.

in the presence of a number of stabilizers are shown in Figure 10. The changes in the IR spectra are shown in Figure 11.

The effect of stabilizers on the photooxidation of polymethylacetylene is generally disappointing. None gave an induction period. Only Irganox 1010 and Tinuvin 770 showed some retardation.

Effect of a Spin Trap. The above results suggest that the autoxidation of poly(methylacetylene) is a free radical chain process. Therefore, we looked for the existence of radicals by EPR. It will be recalled[10] that freshly prepared poly(methylacetylene) is devoid of the $g = 2$ signal that was evident in polyacetylene and copolymers of acetylene and methylacetylene. However, when poly(methylacetylene) is exposed to oxygen at 70 °C for a few minutes, a weak EPR signal developed with $g = 2.0022$ and a line width of 16 G. The intensity of this resonance changed little with the time of oxidation. At 50 °C the resonance doubles its intensity in 60 min. The unpaired spin is apparently very stable; dissolution of the oxidized polymer film in tetrachloroethylene changes neither the line width nor the intensity of the EPR spectra. It seems that the unpaired spin is related to the delocalized neutral defects with restricted mobility[4,19,20] and may or may not play a role in the free radical chain process.

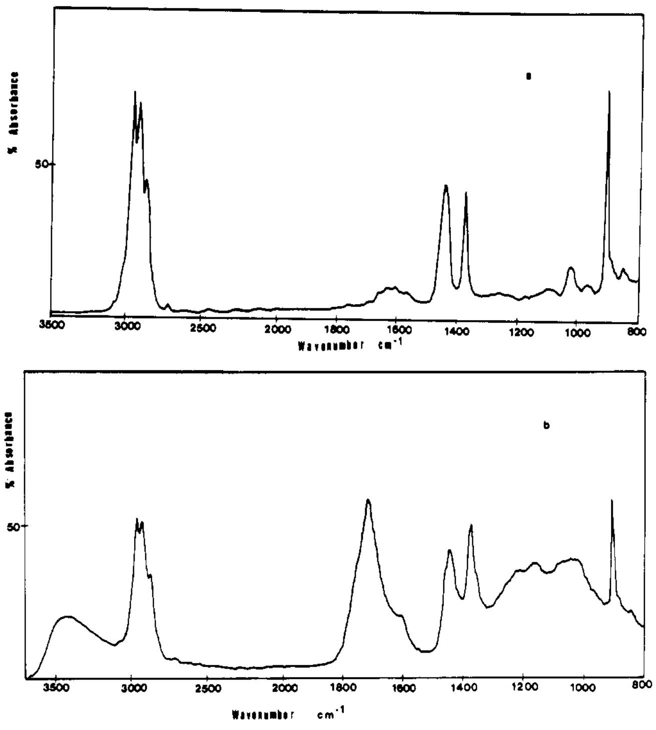


Figure 11. Infrared spectra of (a) poly(methylacetylene) with 1% DMA and (b) after 260 min of irradiation with a mercury lamp under oxygen.

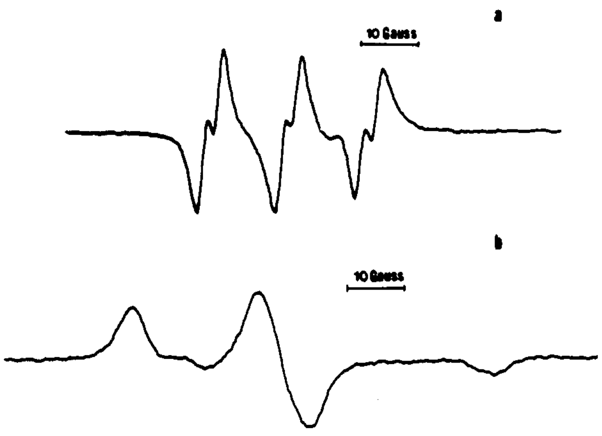
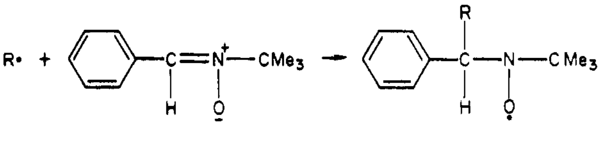


Figure 12. EPR spectra of radical produced during autoxidation of poly(methylacetylene) in the presence of BPN: (a) in toluene solution; (b) in solid polymer film.

In none of the oxidized poly(methylacetylene) was there a detectable signal characteristic of peroxy radicals.[21] Therefore, apparently the peroxy radicals of poly(methylacetylene) are too unstable to be present in a high enough steady-state concentration to be detected by EPR.

A spin trap, *N*-*tert*-butyl-2-phenylnitrone (BPN), was used to detect the concentration of carbon radicals indirectly. A toluene solution of 5% poly(methylacetylene), 2.5% BHT, and 2.5% BPN oxidized with 760 torr of O_2 at 70 °C for 40 min gave the EPR spectrum shown in Figure 12a with nitrogen and proton hyperfine coupling constants of 13.8 and 2 G, respectively. The radical can be attributed to



$$\mathrm{R\cdot} + \mathrm{C_6H_5{-}CH{=}\overset{+}{N}(O^-){-}CMe_3} \rightarrow \mathrm{C_6H_5{-}CH(R){-}N(O\cdot){-}CMe_3} \quad (1)$$

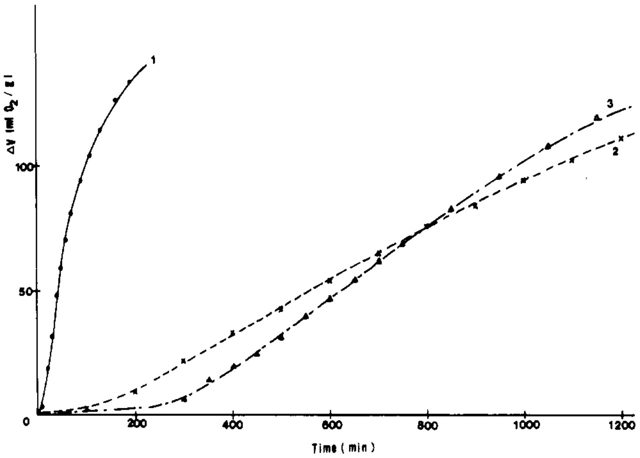


Figure 13. Autoxidation of poly(methylacetylene) at 70 °C and P_{O_2} = 760 torr: (1) 1% BPN; (2) 1% BPN + 1% BHT; (3) 1% BPN + 1% BHT + 1% DSTDP.

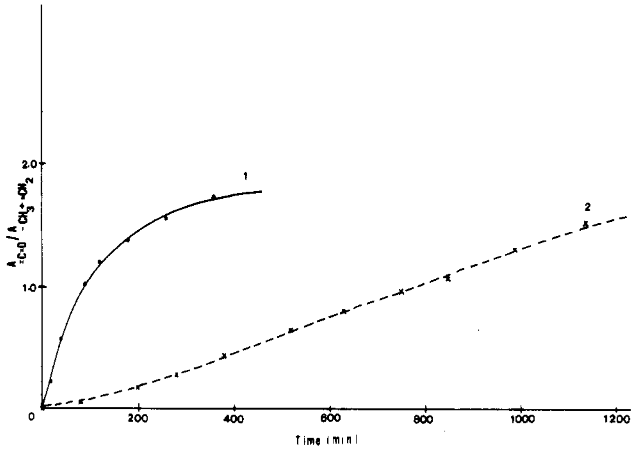


Figure 14. Infrared spectra of autoxidizing poly(methylacetylene) at 70 °C and P_{O_2} = 760 torr: (1) 1% BPN; (2) 1% BPN + 1% BHT.

where R· is a carbon radical of poly(methylacetylene). Figure 12b shows the EPR spectrum of the same radical in polymer film characteristic of it in an immobilized state.

If the carbon radical is the principal chain carrier, then BPN should show an inhibitory effect on the autoxidation of poly(methylacetylene). Curve 1 of Figure 13 shows that BPN by itself has no effect whatsoever; there is no induction period and the maximum rate of oxidation is 11.6 × 10^{-7} mol g^{-1} s^{-1}, which is slightly greater than the value for the unstabilized polymer. This must be interpreted as indicating that the carbon radical is also quite unstable and that BPN only traps a small fraction of it. However, in a synergistic combination with BHT or BHT and DSTDP, BPN enhances the oxidative stability of poly(methylacetylene) (Figure 13). The rates of oxidation were reduced by about a factor of 2 as compared with stabilization by BHT alone. Similar IR evidence of stabilization is shown in Figure 14. The induction period in the oxidation of BHT-stabilized poly(methylacetylene) was increased from 75 to 130 min by the presence of TNP. The spin trap increased the induction periods for the BHT and DSTDP stabilized polymer from 225 to 280 min.

The nitroxide radical concentration as a function of time of oxidation was followed at 70 °C, 1 atm of O_2, and in the presence of 1% BPN and 1% BHT. As soon as the sample reached 70 °C, ca. 10^{-5} mole of spins L^{-1} was observed. During the induction period the concentration remained unchanged. The radical concentration increases as the polymer begins to autoxidize and appears to reach a constant value of 4 × 10^{-5} mol L^{-1} during the period of steady autoxidation (Figure 15).

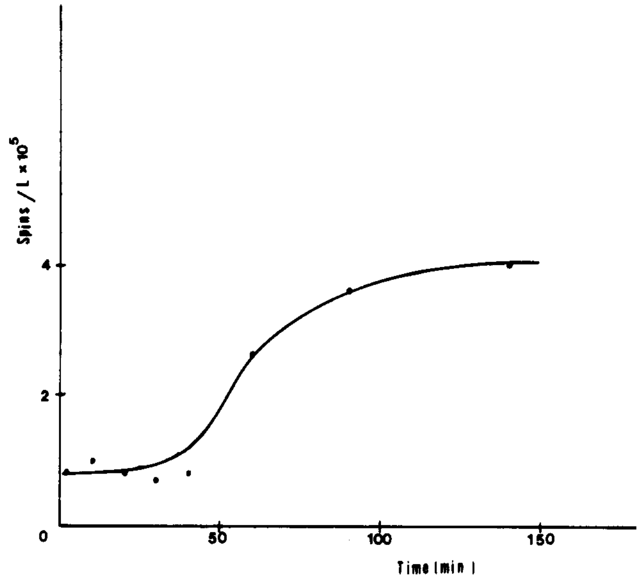


Figure 15. Change of nitroxide radical concentration with oxidation time: 70 °C, P_{O_2} = 760 torr, 1% BPN + 1% BHT.

Discussion of Results

At the outset it is instructive to compare the autoxidation behavior of poly(methylacetylene) with that of other hydrocarbon polymers. As expected, poly(methylacetylene) oxidizes much more rapidly than polyolefins. For instance, the steady state of autoxidation of polypropylene film is 3.6 × 10^{-7} mol g^{-1} s^{-1} at 110 °C whereas the rate is 9.9 × 10^{-7} mol g^{-1} s^{-1} for poly(methylacetylene) at 70 °C. The activation energy for polypropylene oxidation is also greater by comparison, which is about 21.5 kcal mol^{-1} as compared to 14.7 kcal mol^{-1} for poly(methylacetylene). Whereas unstabilized poly(methylacetylene) oxidizes without an induction period, oxidation of polyolefins begins after various periods of induction, depending upon processing, thermal history, and temperature of oxidation. Finally, the rate of poly(methylacetylene) oxidation depends upon the first power of the oxygen concentration, whereas there is no oxygen pressure dependence above 100 torr in the autoxidation of polypropylene in solution and thin films of the polymer.

Poly(methylacetylene) has three allylic protons per monomer unit. One might think that they would play an important role in autoxidation. This is found not to be the case by direct comparison with the autoxidation of polyacetylene.[15] At 70 °C polyacetylene and poly(methylacetylene) have nearly identical autoxidation rates of ca. 9 × 10^{-7} mol g^{-1} s^{-1}. However, the activation energy of polyacetylene oxidation is only about 9.6 kcal mol^{-1}. This shows that the allylic hydrogens, though certainly involved in the autoxidation of poly(methylacetylene), do not play a dominant role in the autoxidation of acetylenic polymers.

Though the present results do not allow definitive statements about the mechanism of autoxidation of poly(methylacetylene), our accumulated knowledge about the autoxidation of polyolefins and polydienes justifies the following speculative discussion.

Initiation Processes. Since poly(methylacetylene) autoxidizes without an induction period and the rate is first order with respect to P_{O_2}, one can assume that oxygen is directly involved in the initiation processes.

It has been demonstrated[5] that oxygen catalyzes the formation of neutral defects or delocalized spins in poly-

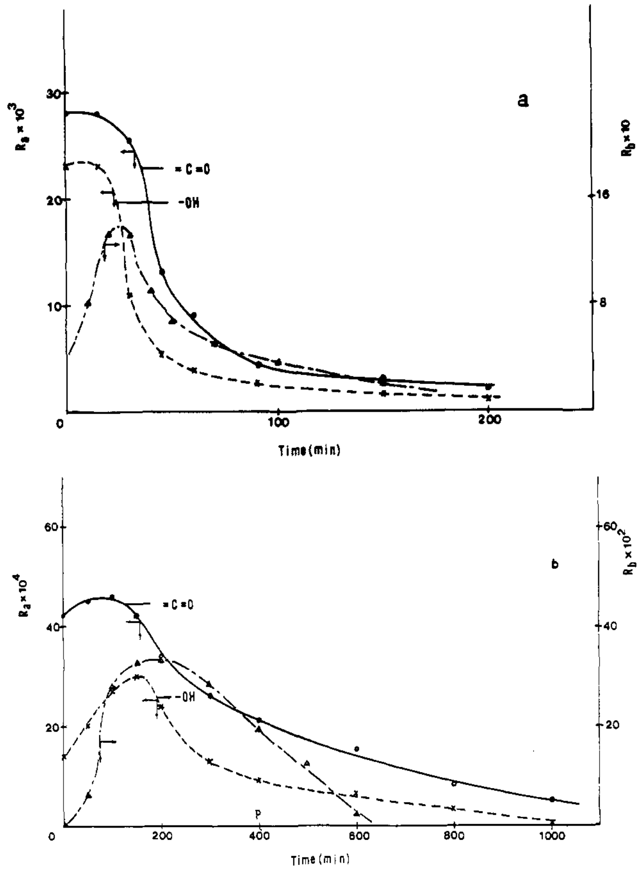
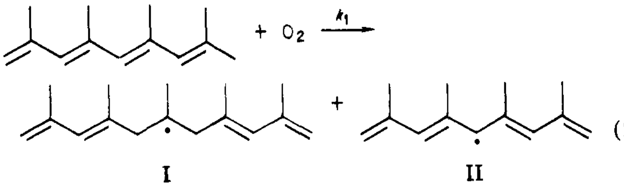


Figure 16. Variation of rates of autoxidation R_b (▲) and of formation R_a of C=O (●) and OH (×) with time of reaction at 70 °C and P_{O_2} = 760 torr: (a) poly(methylacetylene); (b) with 1% BHT.

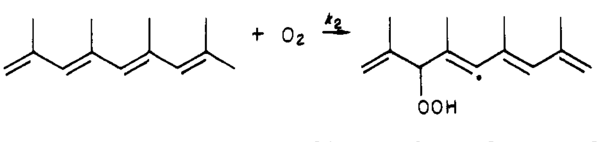
acetylene. The same process may be postulated for poly(methylacetylene) as follows:



(2)

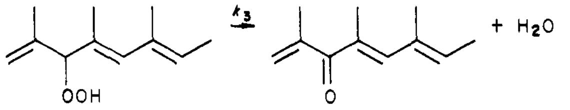
I II

The spins were observed as the weak $g \sim 2$ EPR signal in unstabilized poly(methylacetylene). More convincing evidence is the intense nitroxide signal that appeared in the presence of a spin trap. This may be attributed to reaction 1 where R· is I or II. Another possible direct process is



(3)

This hydroperoxide is probably unstable and may undergo rearrangement as follows:

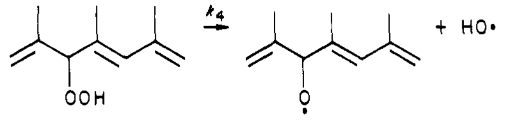


(4)

Reactions 3 and 4 are probably necessary to account for the results shown in Figure 16. The rates of formation of carbonyl and hydroxyl groups are the greatest at the beginning of the oxidation in the absence of an antioxidant. Even with the presence of an antioxidant (Figure 16b), the rates were high during the induction period. Furthermore, Figure 8 showed that the intensity of the OH band reaches a constant value while the carbonyl band intensity continues to increase.

With the low-lying electronic states of poly(methylacetylene) and the presence of unpaired spins, it is possible that there may be excitation of oxygen to the singlet state, i.e., $O_2(\Delta_g)$, especially under UV illumination. The latter can undergo an "ene" reaction to produce hydroperoxides. We do not feel this possibility to be significant because DMA is ineffective as a stabilizer in either thermal oxidation or photooxidation of poly(methylacetylene).

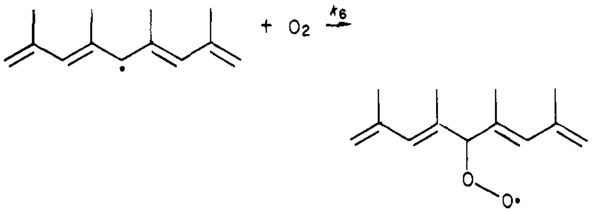
The hydroperoxides produced in reaction 4 and in the subsequent propagation steps will provide a source for secondary initiation, i.e.



(5)

This is the principal initiation reaction in the autoxidation of polyolefins[11-14] and is responsible for the continuation of radical chain processes. On the other hand, reaction 5 does not play a similar important role here. In the oxidation curves shown above, there is either only a slight rate acceleration or none at all. In other words, the rates of reactions 2, 3, and 5 are comparable. Nevertheless, the participation of reaction 5 is supported by the effect of TNP and DSTDP as synergistic hydroperoxide decomposers.

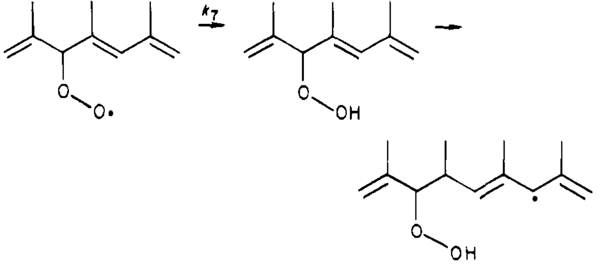
Propagation Processes. The propagation reactions involve R·, RO·, and RO_2· radicals. The main reaction for the R· radical is oxygenation.



(6)

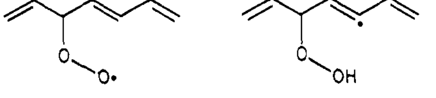
In the case of autoxidation of polyolefins, the corresponding alkyl radicals react with oxygen at diffusion-limited rates. This is probably not true for poly(methylacetylene) because reaction 1 can compete with the oxygenation. If we designate the rate constants for the spin trap reaction to be k_5, then $k_5[\mathrm{BPN}] \gg k_4[\mathrm{O_2}]$.

Several reactions of the RO_2· radical can be visualized

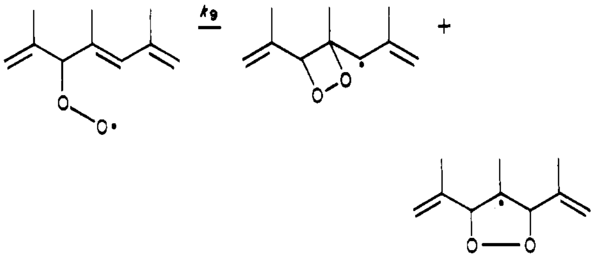


(7)

The $=CH_2$ group vibration occurred between 1300 and 1500 cm^{-1}. Alternative reactions are



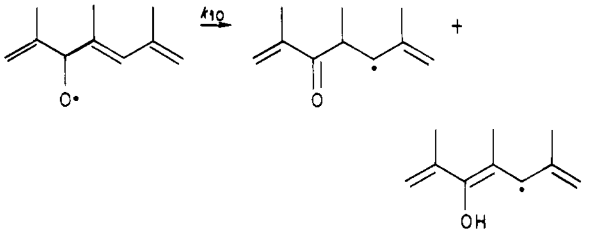
(8)



(9)

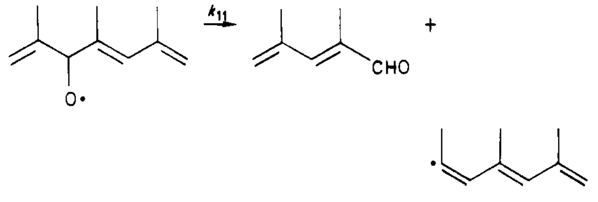
Apparently, $k_8 + k_9 \gg k_7$ because autoxidation of polyacetylene occurs at a comparable rate but with an activation energy smaller than that for poly(methylacetylene).

Dissociation of hydroperoxide yields RO· radicals. The RO· radical is probably immediately converted to carbonyl or hydroxyl products because of the stability of the spin on the backbone



(10)

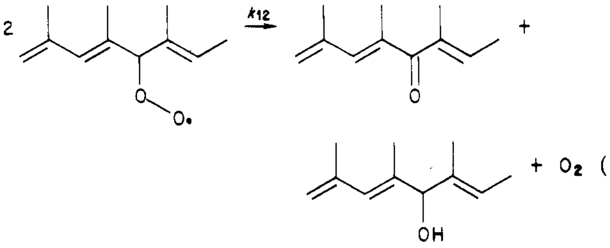
Scission of poly(methylacetylene) can occur by



(11)

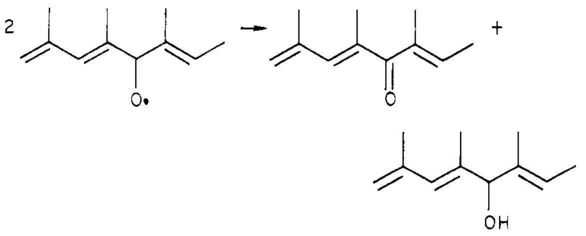
Reactions 7 and 8 given for $RO_2\cdot$ radicals can also have their analogues for the RO· radicals.

Termination Processes. The most probable termination reaction is that between two $RO_2\cdot$ radicals



(12)

Though a similar reaction is possible for the RO· radicals



(13)

probably reactions 10 and 11 supersede reaction 13.

The question of cross-linking reactions for polyacetylene had been posed often because of the insolubility of the polymer and its loss of extensibility upon cis–trans isomerization. Diels–Alder reactions have been proposed.[22] Oxygen was also thought to promote cross-linking. Several reactions may be written for autoxidation which can produce cross-links. However, at least in the case of poly(methylacetylene), the oxidized polymer is soluble in methyl ethyl ketone and tetrahydrofuran. Starting with a poly(methylacetylene) of $\bar{M}_n = 1394$ and $\bar{M}_w/\bar{M}_n = 5.03$, after 27 h of autoxidation at 1 atm of O_2 the oxidized polymer has $\bar{M}_n = 1091$ and $\bar{M}_w/\bar{M}_n = 5.27$. Therefore, there is neither extensive chain scission nor any indication of cross-linking under these conditions.

Kinetics. Oxygen pressure dependence in autoxidation can arise from several causes. At low oxygen pressure when not all terminations occur between two $RO^2\cdot$ radicals (k_{t_1}) but there are also terminations between two R· radicals (k_{t_2}) and cross reactions ($k_{t_{12}}$), then the rate of oxidation is given by

$$-d[O_2]/dt = k_7k_6[RH][O_2]R_i^{1/2}/(k_7k_6k_{t_{12}}[O_2][RH] + 2k_6^2k_{t_1}[O_2]^2 + 2k_7^2k_{t_2}[RH]^2)^{1/2} \quad (14)$$

where [RH] is the polymer concentration and R_i is the rate of initiation. The kinetic order dependence on $[O_2]$ will lie between zero and one, depending upon the relative magnitude of the rate constants and oxygen pressure.

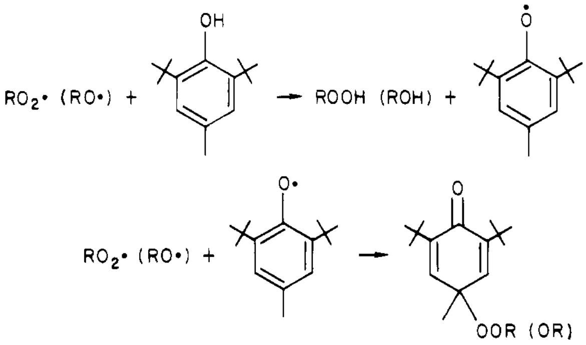
Another source of oxygen pressure dependence is the diffusion limitation for semicrystalline polymers at elevated temperatures and thick specimens.[26] This is not believed to be the case for the very thin films of poly(methylacetylene) oxidized at mild temperatures.

The observed dependence of poly(methylacetylene) autoxidation rate on oxygen partial pressure is best attributed to initiation by oxygen, i.e., reactions 2 and 3. Assuming the steady-state approximation, one finds

$$-d[O_2]/dt = k_2[RH][O_2] + (k_7 + k_8 + k_9)[RO_2\cdot] + k_{12}[RO_2\cdot]^2 \quad (15)$$

The results are consistent with very low $[RO_2\cdot]$ (not detected by EPR) and the importance of reaction 3.

The stabilization of poly(methylacetylene) is most effective when a combination of synergistic stabilizers is used. The RO· and $RO_2\cdot$ radicals can be scavenged by hindered phenols.



(16)

The hydroperoxides were decomposed by phosphorus and sulfur compounds

$$ROOH + R'_3P \rightarrow ROH + R'_3PO \quad (17)$$

and the R· radicals were scavenged by the spin trap.

Acknowledgment. This work was supported in part by grants from NSF, ONR, and DARPA.

Registry No. Poly(methylacetylene), 28391-48-2; *N*-*tert*-butyl-2-phenylnitrone, 3376-24-7; 2,6-di-*tert*-butyl-*p*-cresol, 128-37-0; hydroquinone, 123-31-9; 9,10-dimethylanthracene, 781-43-1; phenylenediamine, 25265-76-3; *N*-phenyl-*N'*-cyclohexylphenylenediamine, 101-87-1; disteryl thiodipropionate, 693-36-7; tris(*p*-nonylphenyl) phosphite, 3050-88-2; bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, 52829-07-9; Irganox 1010, 6683-19-8.

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Analysis of the Complex-Dissociation Model for Free-Radical Copolymerization

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ABSTRACT: Probability theory has been used to derive equations for the complex-dissociation model for free-radical copolymerization showing how the composition, the triad fractions, and the number fractions of sequences in the copolymer are related to the comonomer composition through the reactivity ratios and the equilibrium constant for complex formation. It is shown how these equations can be used to estimate "best" values of the reactivity ratios and the equilibrium constant using experimentally determined copolymer compositions. This model has been applied to the data of Dodgson and Ebdon for the styrene–maleic anhydride copolymerization in bulk at 60 °C. The complex-dissociation model, the penultimate model, and the complex-participation model fit the copolymer/comonomer composition data equally well. However, the predicted styrene sequence distributions of the three models are quite different, and experimental determinations, for example, by ^{13}C NMR, would enable discrimination between the models.

Introduction

Over the past decade considerable interest has been generated in the study of polymerization mechanisms, particularly for systems that have been shown to deviate from the terminal model. Higher order models, such as the penultimate and complex-participation models, have been proposed in order to explain these deviations. Both of these models have been treated mathematically: for example, the work of Alfrey and co-workers[1] and Ham[2] on the penultimate model and of Seiner and Litt[3] and Pittman and Rounsefell[4] on the complex model. We recently reported[5] a probabilistic treatment of the general complex-participation model and described how "best estimates" of the reactivity ratios and the equilibrium constant can be obtained for this model from copolymer/comonomer composition information. We also showed how these copolymerization parameters can be used to predict the number fractions of sequences in the copolymers.

According to the complex-participation model, complexed monomer competes with free monomer in the propagation steps and, when addition of complex takes place, both members of the complex become incorporated in the polymer chain. However, in 1971 Tsuchida and Tomono[6] suggested that, under some circumstances, the complex may be disrupted during the addition step, with only one of the two monomers entering the growing chain. They suggested that this was the case in copolymerization of styrene and maleic anhydride when the complex formed between these two monomers added to a maleic anhydride chain-end radical. They suggested that repulsive forces between the maleic anhydride chain radical and maleic anhydride in the complex was a possible cause for the disruption of the complex during propagation.

These ideas were extended by Karad and Schneider[7] in 1978 when they described what we will call the complex-dissociation model. In this model complex competes with the free monomer in the copolymerization, but the complex is always disrupted in the addition process, and only one monomer component of the complex enters the chain. In their application of this model to the fumaronitrile–styrene copolymerization, Karad and Schneider did not provide a mathematical analysis of the model in its general form but employed a constrained form of the model in which one monomer does not homopropagate through either the free monomer or the complex. This constraint simplified the mathematical analysis of the model but, of course, restricts its application to systems that are known to satisfy this requirement.

For the restricted form of the complex-dissociation model, the mathematical expression for the composition of the polymer is identical in form with that derived by Seiner and Litt[3] for the complex-participation model when this model is constrained so that one monomer does not

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