and unified picture of GC behavior near T_g, and is of use in interpreting the effects of kinetic factors on GC peak shapes.

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Autoxidation of Polyolefins. Absolute Rate Constants and Effect of Morphology

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ABSTRACT: Benzoyl peroxide (BP) has been used to initiate autoxidation of polyolefins from 71 to 105°. The measurements were made for 0.6 to 2% conversion. The initiation efficiency was found to be much lower (by as much as tenfold) for semicrystalline polymer than amorphous polyolefins. The former increases rapidly, approaching the efficiency in the amorphous systems, as the temperature approaches the melting point of the polymer. The difference was attributed to the presence of "encumbered" segments and molecules at the phase boundaries. The "encumbered" radicals probably combine with much higher probability than the radicals of the "free" amorphous molecules. The rate constant ratios $k_p k_t^{-1/2}$ for polypropylene from 130 to 45°, as well as those for model compounds 2,4-dimethylpentane and 2,4,6-trimethylheptane, lie on the same Arrhenius plot. The rate constant of propagation for polypropylene is $k_p = 1.61 \times 10^7 \exp(-12080/RT)(M\ \mathrm{sec})^{-1}$; it is $k_t = 1.11 \times 10^{13} \exp(-11600/RT)(M\ \mathrm{sec})^{-1}$ for the termination process. The values of k_p and k_t for the model compounds appear to fall within experimental errors of these equations. Compared to polypropylene, poly(1-butene) has higher values of k_p and k_t and higher activation energy for propagation. The values of $k_p k_t^{-1/2}$ are nearly the same for poly(4-methyl-1-pentene) as polypropylene. The present work showed that the rate constants reported earlier by us for self-initiated autoxidation of polypropylene are valid.

Over the years there have been many studies on the autoxidation of polyolefins often with contradictory results. This is certainly due to the complexity of the processes and the number of variables involved. Dulog et al.[1] reported the first study of autoxidation of polyethylene (PE), polypropylene (PP), and poly(1-butene) (PB) in trichlorobenzene. For isotactic samples of polypropylene (c-PP) and poly(1-butene) (c-PB) the reaction is autocatalytic and the rate of reaction is proportional to the amount of oxygen absorbed. In contrast, the rate of autoxidation of atactic samples of polypropylene (a-PP) and poly(1-butene) (a-PB) and of PE increases linearly with time and is proportional to the square root of the amount of oxygen absorbed. They attributed the kinetic differences to the isotactic polymers having conformations favoring intramolecular propagation but not for the atactic or syndiotactic polymers. The overall activation energies are about 7–8 kcal mol^{-1} greater for the amorphous polymers than the corresponding crystalline polyolefins. That the chain conformations of isotactic and atactic polyolefins in solution at temperatures between 120 and 176° should be different is both unexpected and surprising. In a more recent study by van Sickle,[2] the autoxidations of both amorphous and crystalline polypropylene in benzene solution from 100 to 130° were found to be very similar. The reaction rate is proportional to $[\mathrm{initiator}]^{0.58}[\mathrm{polypropylene}]^{0.73}$ and is independent of reaction time. Up to half of the oxygen consumed was found to be hydroperoxides. On the other hand, the rate of autoxidation of a-PP in solution was found by Bawn and Chandhri[3] to depend upon $[\mathrm{polypropylene}]^{1.7}[\mathrm{O_2}]^1$ both in uncatalyzed systems[3a] and in reactions catalyzed by manganese salts.[3b] The dependence on oxygen pressure in the range of 450 to 750 Torr for autoxidation in solution is unusual. Fractional kinetic order for autoxidation of polypropylene was also observed by Niki et al.[4] who found the rate to be proportional to $[\mathrm{polypropylene}]^{0.44}[\mathrm{initiator}]^{0.68}$. These authors concluded that even though intramolecular propagation is favored, its chain length is short.

The autoxidation of model hydrocarbons appears to be uncomplicated; the kinetics are simply first order in the substrate concentration and half-order in the initiator concentration. Intramolecular propagation, k_p, is favored over the intermolecular propagation, k_p'. The ratio of $k_p/k_p' \approx 66\ M$ for both 2,4-dimethylpentane[5,6] and 2,4,6-trimethylheptane[7,8] with the dihydroperoxide and the trihydroperoxide, respectively, as the major products.

One faces a number of technical difficulties in studying autoxidation of bulk polymers. The sample thickness is important; oxidation occurs less rapidly and is less extensive in the interior of thick samples.[9,10] For semicrystalline polymers, the initial stage of oxidation is confined primarily to the amorphous phase.[11,12] If volatile oxidation products are not removed, autoxidation is greatly accelerated.[13,14] Other contributing factors are degree of branching,[15] amount of unsaturation,[16] and molecular weight distribution.[17]

Two areas have been the main focal points of researches. What are the products of autoxidation and what are the kinetics of the process?

Neiman and coworkers[18,19] measured the accumulation of hydroperoxides and other oxidation products of PP using ir, GLC, polarography, and other chemical methods. Matveeva et al.[20] showed that many products can be accounted for as decomposition products of hydroperoxides. Acetic acid, formic acid, and acetone were found to be major volatile oxidation products of PE and PP; this led Bevilacqua et al.[21,22] to suggest intramolecular propagation. Chien and coworkers[23,24] found that a major portion of the hydroperoxides produced in the oxidation of PE and PP dissociate much faster than the rest. Using a combination of chemical and spectroscopic techniques, these authors[25] showed that about 75% of these are ajacent dihydroperoxides and trihydroperoxides of polypropylene. Zolotova and Denisov[26] have synthesized both adjacent and isolated hydroperoxides of PE and PP. Adams[27] had identified γ-lactones in oxidized PP thus furnishing further evidence for intramolecular back-biting propagation. It seems that this process is beyond doubt an important one for the autoxidation of poly(α-olefins). The formation of adjacent hydroperoxides has also been firmly established. By virtue of their ease of decomposition, they are probably the principal initiation species at moderate temperatures. However, the debate about how long this sequence can be still goes on. The sequence length would most certainly be dependent on the experimental conditions.

A number of kinetic studies have been made on the autoxidation of polyolefins.[28-31] However, not until Chien and Boss[32] combined electron spin resonance (ESR) with several other techniques were the rate constants for initiation, propagation, and termination determined. This technique has also been used recently by Niki et al.[33] Our earlier work on uncatalyzed autoxidation has been criticized for high conversion and possible secondary oxidations.[34,35] In this paper, we used an initiated system to determine rate constants for the autoxidation of various polyolefins carried out to low conversions. The effect of polymer morphology on the individual processes is also examined and reported here.

Experimental Section

Materials. Benzoyl peroxide (BP) from Fischer Chemicals as purified by repeated recrystallizations from chloroform-methanol and subsequently vacuum dried at ambient temperature. The product has a mp of 104–104.5°. To be used as an inhibitor, 2,6-*tert*-butyl-*p*-cresol (AH) was obtained from Aldrich Chemical Co. and purified by repeated recrystallizations from methanol. It has a mp of 69°.

Benzene, cumene, squalane, and *n*-heptane (Eastman Organic Chemicals) were purified by prolonged stirring with concentrated H_2SO_4. The colored acid was replaced with fresh acid. The procedure was repeated until the acid layer remained colorless overnight. The solvents were then washed, neutralized, washed again, dried over $CaCl_2$, and fractionated. The central cuts of benzene, *n*-heptane, cumene, and squalane (the last two at reduced pressure), have $n^{20}D$ values of 1.5008, 1.3872, 1.4910, and 1.4525, respectively. Eastman Organic chlorobenzene was dried over Dririte and distilled shortly before use ($n^{20}D$ = 1.5244). Spectral grade methanol (MCL Laboratories), CCl_4 (Fischer), and acetone (Aldrich) were used as received.

Amorphous polypropylene (unstabilized Eastobond M-5L, TX-320-34) was twice purified by reprecipitation from chlorobenzene solution with acetone and vacuum dried at ambient temperature. The infrared spectrum of a 4-mil film of this purified a-PP showed little absorption at 996 cm^{-1} alongside the strong absorption at 974 cm^{-1}. The polymer is estimated to contain less than 2% isotactic polypropylene.[36] It has a density of 0.867 g cm^{-3} at 23° (lit.[37] 0.87 g cm^{-3}) and a melt viscosity of 3370 cP at 190°. Profax 6501 c-PP has a crystallinity of 61% (vide infra). Processing stabilizers in the polymer flake were extracted with methylene chloride for 2 days under nitrogen using a Soxhlet apparatus and then vacuum dried for two more days. The mp of the c-PP is 165°. Poly(1-butene) (Mobil PB-001) designated as c-PB was freed of additives by dissolution in hot toluene, filtered, and precipitated with acetone, after which the product was successively extracted with methylene chloride for 48 hr and anhydrous ether for 24 hr to remove low molecular weight fractions. Upon drying to constant weight the purified c-PB has a density of 0.908 g cm^{-3} at 23° and a mp of 112°. It has a crystallinity of about 50%. Poly(4-methyl-1-pentane) (PMP) was obtained from Hercules, Inc. After 48 hr of methylene chloride extraction and drying, the material melts at about 240° and is about 30% crystalline (vide infra).

Determination of Crystallinity. The degree of crystallinity (X_c) of the polyolefin sample was determined with an ethanol-water density gradient column. From the observed density p, the value of X was calculated by

$$X_c = \left(\frac{P - P_a}{P_c - P_a}\right)\left(\frac{P_c}{P}\right) \qquad (1)$$

where P_c and P_a are the crystalline and amorphous densities, respectively, given in the literature.[37,38]

The densities of the amorphous and the crystalline phases of PMP are nearly the same. Therefore, X_c was determined calorimetrically with a Perkin-Elmer Model DSC-2 differential scanning calorimeter. The procedure used was given by Miller.[38] The ratio of the observed enthalpy of fusion to the enthalpy of fusion of completely crystalline c-PMP gives X_c. The latter was given by Isaacson et al.[39] to be 33.9 cal g^{-1}.

Sample Preparation. Thin films of a-PP were cast from a 10% benzene solution on a Teflon sheet. After evaporation in the absence of light, the samples were vacuum dried for 2 days. The film, 4 to 5 mil in thickness, showed no ultraviolet absorption characteristic for benzene.

Thin films of c-PB and c-PMP were similarly casted from a 5% and a 1.6% CCl_4 solution, respectively. Extract of the finished film with acetone showed no absorption at 770 cm^{-1} characteristic for CCl_4.

When initiator and/or inhibitor were added to the polymer solution, the actual amounts present in the film after evaporation and drying were separately determined. A piece of polymer film was weighed (~0.6 g) and cut into small pieces. BP was extracted with 3 ml of acetone for 1 week and its concentration was determined from the absorbance at 278 nm (ϵ = 2000 M^{-1} cm^{-1}).

Films of c-PP were prepared with a Carver laboratory press with a 3-mil aluminum spacer at 210° and 15000 psi for 5 min. The sample which was cooled naturally while in the press is designated c-PP-S; it has a density of 0.917 g cm^{-3} and is about 71% crystalline. Other samples were quenched in dry ice-acetone both to give c-PP-Q which has a density of 0.887 g cm^{-3} and are about 44% crystalline.

Additives were introduced into the polypropylene films after the films were formed. This was accomplished by swelling of finely cut c-PP films in benzene solution saturated with BP and appropriate quantities of AH for 3 weeks. The sample was subsequently washed with acetone and vacuum dried for 7 days at ambient temperature. The content of PB was determined by iodimetry; the content of AH was determined as described above.

Decomposition of Benzoyl Peroxide. The rate of decomposition of BP in polymer films was followed by the absorbance of the 998-cm^{-1} band which has been assigned to the 0–0 stretching vibration.[40,41] The polyolefin films were sufficiently transparent in this region for good sensitivity. The optical densities of 4-mil PP, 5-mil PB, and 3-mil PMP are 0.15, 0.20, and 0.10, respectively. A film, free of additives, carefully selected for matching thickness, was used as the reference. The samples were aged in a thermostated oven (±0.21°) with air circulation. Within the temperature range of 71 to 92° of this study, the films suffered no significant distortion or changes in thickness. The polymer bands at 981, 905, and 933 cm^{-1}, respectively, for PP, PB, and PMP did not change in intensity during the course of an experiment.

Autoxidation Procedure. The autoxidation procedure and the continuous recording automatic oxygen up-take apparatus have

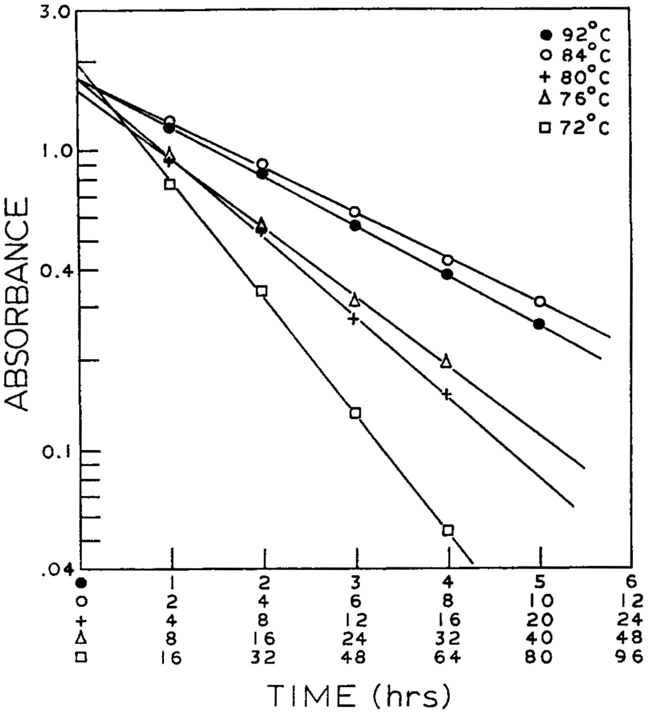

Figure 1. Log optical density (998-cm^{-1} band) vs. time plots for the decomposition of BP in a-PP in the presence of air: $[BP]_0 = 0.127\,M$, $[AH]_0 = 7.4\,mM$.

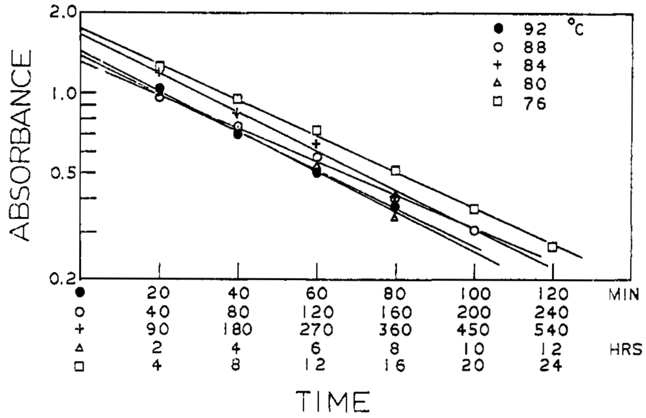

Figure 2. Log optical density (998-cm^{-1} band) vs. time plots for the decomposition of BP in c-PB in the presence of air, $[BP]_0 = 0.376\,M$.

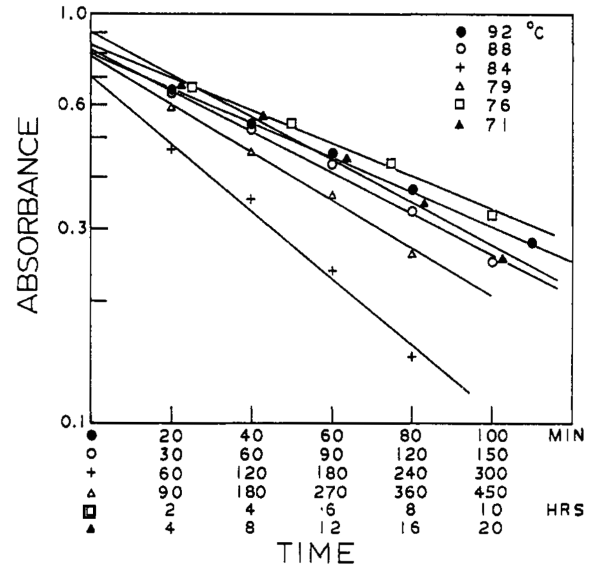

Figure 3. Log optical density (998-cm^{-1} band) vs. time plots for the decomposition of BP in c-PMP in the presence of air: $[BP]_0 = 0.33\,M$, $[AH]_0 = 29\,mM$.

been given previously.[42,43]

Because the dissociation of BP liberates varying amounts of CO_2 depending upon experimental conditions, some autoxidation runs were repeated exactly except N_2 was present instead of O_2. The volume of gas liberated in the latter run was used to correct the gas volume change measured in the former to obtain the true up-take of oxygen. In other runs NaOH pellets were suspended over the polyolefin sample to absorb CO_2. The results of the two kinds of measurements agree to better than 5%.

Electron Spin Resonance (ESR). The procedure used to determine peroxy radical concentrations in an autoxidizing sample has been described elsewhere.[32,44] The radical concentration was calculated from the following equation,[45]

$$[PO_2] = [S]\left(\frac{A_{PO_2}}{A_s}\right)\left(\frac{G_s}{G_{PO_2}}\right)\left(\frac{V_s}{V_{PO_2}}\right)\left(\frac{P_s}{P_{PO_2}}\right)^{1/2} \qquad (2)$$

where A is the double integrand of the EPR spectrum, G is the spectrometer gain, V is the effective sample size, and P is the microwave power. Subscript s refers to a DPPH standard and PO_2 refers to the polymer sample. The double integration was performed by a computer program written according to the method of Wyard.[46]

Results

Decomposition of Benzoyl Peroxide in Polyolefin Matrices. BP has been used extensively as an initiator for free-radical polymerization[47-50] and autoxidation of hydrocarbons[51,52] and polyolefins.[53] The decomposition process can be rather complicated involving radical-induced reactions[54,55] which are solvent dependent. However, the process is greatly simplified and becomes first order in kinetics in the presence of either oxygen or radical chain inhibitors.[56-59] This is because the free radicals react much faster with O_2 and inhibitors than with BP.

The rate of decomposition of BP in polyolefins follows first-order kinetics. Typical data for PP, PB, and PMP are shown in Figures 1, 2, and 3, respectively. These semilog plots of optical density at 998 cm^{-1} vs. time are linear up to four half-lives. The rate constants of dissociation are summarized in Table I. They are independent of added inhibitor supporting the absence of radical-induced decomposition of BP in these experiments. Arrhenius plots of the data (Figures 4–6) gave activation parameters summarized in Table II along with those reported by other workers. The values are in substantial agreement.

It should be mentioned that two other initiators azobis(isobutyronitrile), AIBN, and Lauroyl peroxide, LP, were also extensively studied in a-PP. At concentrations less than 0.085 M, the dissociation of AIBN is first order for about 2 half-lives. At higher concentrations (>0.15 M) the process is autocatalytic resembling that for crystalline AIBN samples. Only at the lowest concentration does the value of k_d in a-PP approach those in liquid. The results indicate incompatibility of AIBN in a-PP. Similar behavior was seen with LP in a-PP. Phase separation and radical-induced decomposition were unavoidable for these two systems except at very low initiator concentrations. Therefore, these initiators were unsuited for our purpose.

Initiation Efficiency of Benzoyl Peroxide in Polymer Matrices. For free-radical reactions in liquids, the efficiency of an initiator is decreased by primary cage combinations.[63] The fraction of radicals which did not undergo cage combination is $1 - \alpha$. They can be efficiently captured by suitable reagents. The efficiency of radical generation, α, should decrease rapidly with the increase of viscosity.

Table I
Dissociation of Benzoyl Peroxide in Polyolefin Matrices

	Polypropylene			Poly(1-butene)			Poly(4-methyl-1-pentene)		
Temp, °C	$[BP]_0$, mM	$[AH]_0$, mM	$k_d \times 10^5$, sec^{-1}	$[BP]_0$, mM	$[AH]_0$, mM	$k_d \times 10^5$, sec^{-1}	$[BP]_0$, mM	$[AH]_0$, mM	$k_d \times 10^5$, sec^{-1}
71	0.127	7.4	1.56				0.33	29	1.67
76	0.127	7.4	1.85	0.376	0	2.09	0.33	29	2.51
80	0.064	3.5	4.1	0.376	0	4.84	0.33	0	4.91
80	0.127	7.4	4.0	0.376	12.5	4.78	0.33	29	4.91
80	0.251	13.7	4.1						
84	0.127	7.4	4.81	0.376	0	6.42	0.33	0	7.7
84	0.251	13.7	4.96				0.33	29	9.6
88	0.064	3.5	10.5	0.376	0	11.6	0.33	0	9.24
88							0.33	29	12.0
92	0.127	7.4	12.0	0.55	0	12.8	0.33	29	20

Table II
Rate Constants of Dissociation of Benzoyl Peroxide in Polymer Matrices

Polymer	Temp range, °C	k_d, sec^{-1}	Method	Ref
Polypropylene	71–92	$8.4 \times 10^{13} \exp(-29700/RT)$	Ir	This work
Polypropylene	65–87	$4.5 \times 10^{13} \exp(-29800/RT)$	Iodimetry	60
Poly(1-butene)	71–92	$8.4 \times 10^{13} \exp(-29700/RT)$	Ir	This work
Poly(4-methyl-1-pentene)	71–92	$7 \times 10^{13} \exp(29300/RT)$	Ir	This work
Poly(ethyl acrylate)	85–110	$8 \times 10^{13} \exp(-29600/RT)$	CO_2 evolution	53
Poly(styrene)	>82	$6.73 \times 10^{13} \exp(-30100/RT)$	Ir	61
Poly(carbonate)	86–100	$5.5 \times 10^{13} \exp(-30000/RT)$	Iodimetry	62

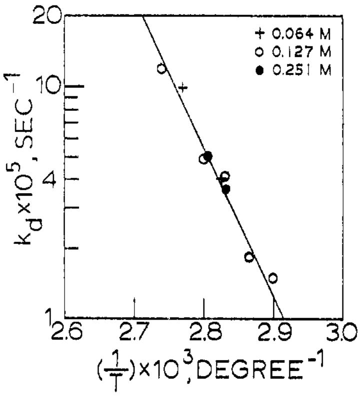

Figure 4. Arrhenius plot for the decomposition of BP in a-PP.

Various quantities of AH were added to polyolefins containing BP and the induction period, t_{ind}, as well as the rate of oxidation during this period, R_{ind}, were measured. The results for a-PP, c-PB, and c-PMP are given in Tables III to V. The initiation efficiency is defined as

$$BP \xrightarrow{k_d} 2\alpha R \quad (3)$$

and is obtained from

$$\alpha = [AH]_0/[BP]_0(1 - e^{-k_d t_{ind}}) \quad (4)$$

The values of k_d are those given in Table I. It is assumed throughout this paper that all the additives are found in the amorphous phase. This assumption is however unnecessary for the calculation of α, since $[AH]_0$ and $[BP]_0$ appear in the numerator and denominator, respectively. In eq 3 it is also assumed that each AH scavenges two radicals.[64,65] However, anomalous stoichiometries have been observed in certain systems.[42]

The values of α in a-PP increase linearly with temperature as shown in Figure 7. In comparison, the initiation efficiency of BP in c-BP is much smaller compared to that in a-PP at the same temperatures, the value beginning to increase rapidly above 90°. It is interesting that the two curves meet at 114° when extrapolated by 5–10°. It is recalled that the purified c-PB has a mp of 112°. This behavior showed that initiation is markedly less efficient in a semicrystalline polymer than in an amorphous polymer. A few measurements on c-PP also show this difference. For example, at 85°, the quenched sample c-PP-Q has α = 0.10 and the slowly cooled sample c-PP-S has α = 0.08. Both these values are significantly smaller than for a-PP at the same temperature.

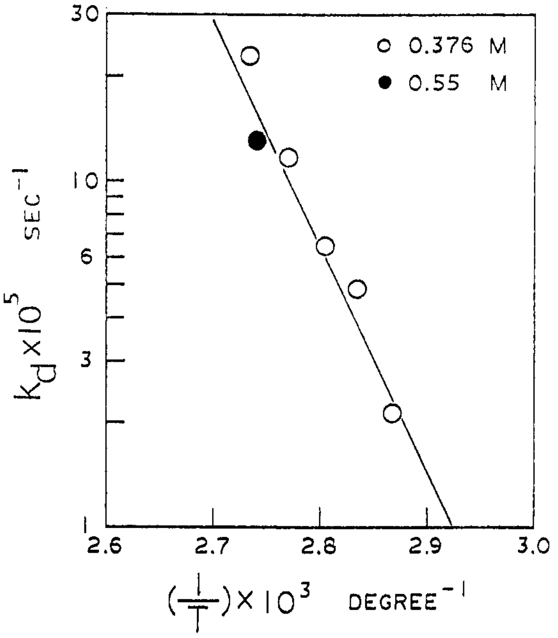

Figure 5. Arrhenius plot for the decomposition of BP in c-PB.

It is also noted that there is significant oxygen consumption during the induction period.

Benzoyl Peroxide Initiated Autoxidation of Polyolefins. The data for the autoxidation of polyolefins are summarized in Tables VI to IX. The steady-state rate of oxida-

Table III
Initiation Efficiency of Benzoyl Peroxide in Amorphous Polypropylene[a]

Temp, °C	$[AH]_0$, mM	t_{ind}, min	α	$R_{ind} \times 10^6$, M sec^{-1}
71	7.4	630	0.14	0.98
71	7.4	600	0.15	0.95
76	6.8	260	0.17	1.21
76	3.4	120	0.19	2.12
76	3.7	140	0.17	2.03
76	7.4	275	0.18	
80	7.4	105	0.26	5.26
80	7.4	105	0.26	4.95
85	11.0	60	0.34	8.13
90	15.0	50	0.39	14.8
95	26.5	40	0.48	
100	40.7	30	0.54	
105	72.6	30	0.62	

[a] 0.6 of 4-mil a-PP film containing 0.127 BP, $P_{O_2} = 1$ atm.

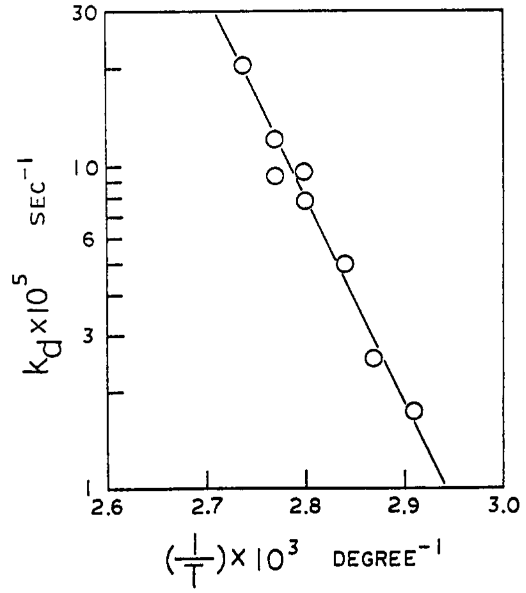

Figure 6. Arrhenius plot for the decomposition of BP in c-PMP.

tion, R, is calculated assuming that only the amorphous phase is oxidized. Conversions for these experiments range from 0.6 to 2%.

In these tables β is the kinetic chain length,

$$\beta = R(2\alpha k_d[BP]_0 e^{-k_d t})^{-1} \quad (5)$$

The rate constant ratio $k_p k_t^{-1/2}$ is obtained from the rate of oxidation by the equation

$$R = \alpha k_d[BP]_0 e^{-k_d t} + \frac{k_p}{k_t^{1/2}}[PH](2\alpha k_d[BP]_0 e^{-k_d t})^{1/2} \quad (6)$$

The values of α were given in Tables III to V. A simplifying assumption is that only the tertiary hydrogens were abstracted; their concentrations are 21, 20, and 16 M respectively for PP, PB, and PMP. Whereas only the amorphous phases of PP and PB were assumed to be oxidized, we did not make the same assumption for PMP. At room temperature the crystalline phase of PMP is less dense than the amorphous phase; they have the same density at about 60°. Winslow and Matreyek[66] had previously pointed out that both phases are oxidized. In our calculation of $k_p k_t^{-1/2}$ for PMP, the back-bone and side-chain tertiary hydrogen are assumed to have the same reactivity; however, we note that the former has been said to be more reactive than the latter.

Table IV
Initiation Efficiency of Benzoyl Peroxide in Poly(1-butene)[a]

Temp, °C	$[AH]_0$, mM	t_{ind}, min	α	$R_{ind} \times 10^6$, M sec^{-1}
76	3.0	500	0.018	0.58
80	3.0	210	0.022	1.85
85	3.0	75	0.03	6.91
85	4.6	125	0.03	
88	4.6	60	0.04	
90	6.4	55	0.049	17.2
95	4.4	10	0.11	
95	14.2	22	0.15	
100	13.5	12	0.3	
100	22.3	20	0.3	
105	50.3	20	0.43	
110[b]	70.8	14	0.59	

[a] 0.3 to 0.6 g of 5-mil c-PB film containing 0.376 M of BP, $P_{O_2} = 1$ atm. [b] $[BP]_0 = 0.188$ M.

Table V
Initiation Efficiency of Benzoyl Peroxide in Poly(4-methyl-1-pentene)[a]

Temp, °C	$[AH]_0$, mM	t_{ind}, min	α	$R_i \times 10^6$, M sec^{-1}
85	2.0	90	0.012	5.15
85	2.8	100	0.015	5.30
90	5.0	60	0.025	18.8
90	14.0	120	0.035	17.5
92.5	10.4	75	0.037	30.8
95	14.0	55	0.05	44.3

[a] 0.3 g of 2.5-mil c-PMP film containing 0.33 M of BP, $P_{O_2} = 1$ atm.

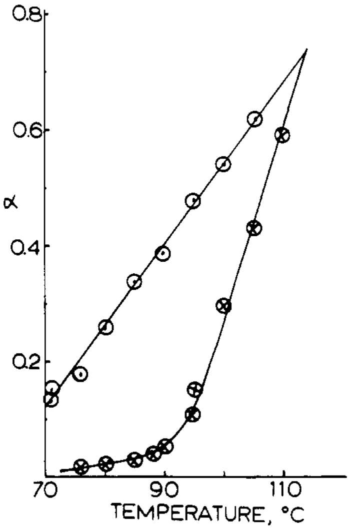

Figure 7. Variation of α for BP as a function of temperature: (⊙) in a-PP; (⊗) in c-PB.

The results of $k_p k_t^{-1/2}$ are also given as Arrhenius plots in Figures 8–10. The values of Chien and Boss[32] and Niki et al.[33] for polypropylene are also included in Figure 8. They all are found near the same line.

Electron Spin Resonance of Autoxidizing Polyolefins. ESR has been used by us previously[32] in the determination of rate constants for polypropylene oxidation. Only the peroxy radicals can be detected, the lifetime of which is long (~10^{-2} sec). The lifetime of the alkoxy radical is shorter than 10^{-8} sec;[68,69] it cannot be detected even at very low temperature when generated photolytically.[44] As far as we know ESR spectrum of an aliphatic alkoxy radical has not yet been observed.

Table VI
Benzoyl Peroxide Initiated Autoxidation of Amorphous Polypropylene[a]

Temp, °C	$[AH]_0$, mM	$R \times 10^5$, M sec^{-1}	$k_pk_t^{-1/2} \times 10^4$, $(M \text{ sec})^{-1/2}$	β
71	7.4	0.55	5.03	20.7
71	7.4	0.63	5.20	20.0
76	0	1.10	5.25	11.5
76	6.8	1.03	5.99	15.8
76	3.4	1.06	5.31	12.1
76	3.7	1.09	5.89	14.0
76	7.4	1.03	5.88	15.1
80	7.4	1.85	6.15	9.6
80	7.4	1.77	5.86	9.1
85	0	3.50	6.20	5.8
85	11.0	3.22	6.80	6.5
90	0	6.25	8.80	5.0
90	15.0	6.45	7.20	5.5
95	0	10.2	9.22	4.2
95	26.5	7.08	8.03	4.6
100	0	17.5	10.5	3.3
105	0	26.1	11.5	2.8

[a] 0.6 g of 4-mil film containing 0.127 M of BP, P_{O_2} = 1 atm.

Table VII
Benzoyl Peroxide Initiated Autoxidation of Poly(1-butene)[a]

Temp, °C	$[AH]_0$, mM	$R \times 10^5$, M sec^{-1}	$k_pk_t^{-1/2} \times 10^4$, $(M \text{ sec})^{-1/2}$	β
76	0	0.32	3.75	12.0
76	3.0	0.29	4.65	18.0
80	0	0.82	6.51	14.0
80	3.0	0.52	5.10	13.5
85	0	2.08	9.82	12.6
85	3.0	1.38	7.70	11.5
85	4.6	1.21	7.51	13.0
90	0	4.24	12.6	11.0
90	6.4	3.74	13.1	13.0
95	4.4	12.4	19.0	9.0
95	14.2	11.5	17.0	8.0
95	0	13.8	17.8	6.4
100	0	22.7	26.4	7.0
105	0	52.0	33.0	6.0
110	0	126.0	55.0	7.0

[a] 0.3 to 0.6 g of 5-mil film containing 0.376 M of BP for experiments at 95° and lower, it is 0.188 M in runs 100° and higher, P_{O_2} = 1 atm.

The concentrations of PO_2 radicals found in autoxidizing polypropylene and poly(1-butene) are given in Tables X and XI, respectively. In these tables, k_t is obtained from the PO_2 concentration by

$$k_t = 2k_d[BP]_0[PO_2]^{-2}e^{-k_dt} \quad (7)$$

and k_p is calculated from the values of k_t and $k_pk_t^{-1/2}$ given in the previous tables.

Discussion of Results

Initiation Efficiency and Polymer Morphology. The large differences between the abilities of radicals to escape cage combination in various polyolefins are most likely the consequence of morphology.

The chain conformation of molecules in bulk amorphous polymers has now been shown by low-angle neutron scattering to be the same as that in θ solvent.[70-72] The chain conformation in molten crystallizable polymer, such as polyethylene, does not, however, have the unperturbed dimension.[73]

Table VIII
Benzoyl Peroxide Initiated Autoxidation of Poly(4-methyl-1-pentene)[a]

Temp, °C	$[AH]_0$, mM	$R \times 10^5$, M sec^{-1}	$k_pk_t^{-1/2} \times 10^4$, $(M \text{ sec})^{-1/2}$	β
85	2.0	0.96	6.88	13.8
85	2.8	0.90	6.03	16.7
85	0	1.20	5.90	13.0
85	0	1.51	7.60	15.8
90	5.0	2.57	9.80	16.4
90	14.0	2.10	9.50	17.8
90	0	3.75	9.60	10.5
92.5	10.4	3.05	10.5	14.8
92.5	0	4.51	9.72	9.3
95	14.0	4.32	10.8	11.1
95	0	6.92	11.1	7.6
95	0	7.21	12.0	7.9

[a] 0.3 g of 2.5-mil film containing 0.33 M of BP, P_{O_2} = 1 atm.

Table IX
Benzoyl Peroxide Initiated Autoxidation of Isotactic Polypropylene at 85°[a]

Sample	$[BP]_0$, M	$[AH]_0$, mM	$R \times 10^5$, M sec^{-1}	$k_pk_t^{-1/2} \times 10^4$ $(M \text{ sec})^{-1/2}$	β
c-PP-Q	0.017	0	0.27	6.80	11
c-PP-Q	0.017	0.88	0.21	5.0	15
c-PP-S	0.028	0	0.42	6.6	12
c-PP-S	0.028	1.44	0.39	7.1	16

[a] 0.6 g of 3–4-mil film, P_{O_2} = 1 atm.

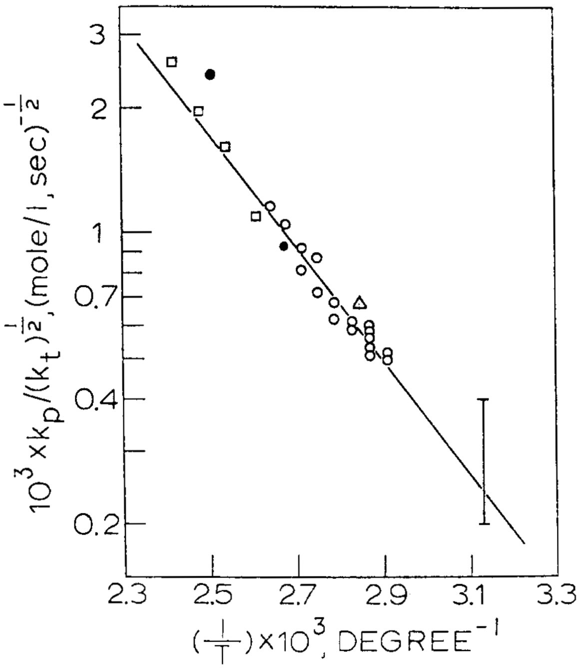

Figure 8. Values of $k_pk_t^{-1/2}$ as a function of T^{-1} for oxidations of polypropylenes and model compounds: (○) a-PP initiated by BP (this work); (□) c-PP self-initiated (ref 32); (I) a-PP initiated by di-*tert*-butyl peroxyoxalate (ref 33); (●) 2,4-dimethyl pentane (ref 6); (△) 2,4,6-trimethylheptane (ref 7).

The morphology of semicrystalline polymer is of course more complicated. For many properties, a two-phase model seems to be adequate. This model is however incapable of explaining the autoxidation results presented above. The morphology of semicrystalline polymer is intimately related to the origin of the amorphous component in polymer single crystals and the nature of the fold surface.[74] While this question is far from resolved, it is reasonable to assume that the single crystals are imperfect and have at the surfaces either folds which are long and loose,[75,76] with cilia and nonadjacent reentry loops,[77] or physically adsorbed

Table X
Rate Constants of Benzoyl Peroxide Initiated Autoxidation of Amorphous Polypropylene[a]

Temp, °C	$[PO_2] \times 10^6$, M	k_p, $(M\ sec)^{-1}$	$k_t \times 10^{-6}$, $(M\ sec)^{-1}$
90[b]	4.05	0.88	1.21
	4.30	0.83	1.07
	Av. 4.18 ± 0.2	0.85 ± 0.04	1.13 ± 0.1
95[c]	5.20	1.10	1.62
	6.12	0.94	1.17
	5.90	0.97	1.26
	5.63	1.02	1.38
	Av. 5.71 ± 0.6	1.01 ± 0.07	1.36 ± 0.2
100[d]	7.68	1.27	1.47
	8.36	1.20	1.30
	7.92	1.26	1.44
	7.22	1.39	1.74
	Av. 7.80 ± 0.6	1.28 ± 0.08	1.49 ± 0.2
105[e]	9.42	1.55	1.81
	8.72	1.67	2.12
	Av. 9.07 ± 0.5	1.61 ± 0.08	1.97 ± 0.2

[a] Sample with 0.254 M of BP was oxidized at 1 atm of O_2. [b] $\alpha = 0.39$, $k_d = 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 8 \times 10^{-4} (M\ sec)^{-1/2}$. [c] $\alpha = 0.48$, $k_d = 1.8 \times 10^{-4}$, $k_pk_t^{-1/2} = 8.65 \times 10^{-4}\ (M\ sec)^{-1/2}$. [d] $\alpha = 0.54$, $k_d = 3.3 \times 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 1.05 \times 10^{-3}\ (M\ sec)^{-1/2}$. [e] $\alpha = 0.62$, $k_d = 5.1 \times 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 1.15 \times 10^{-3}\ (M\ sec)^{-1/2}$.

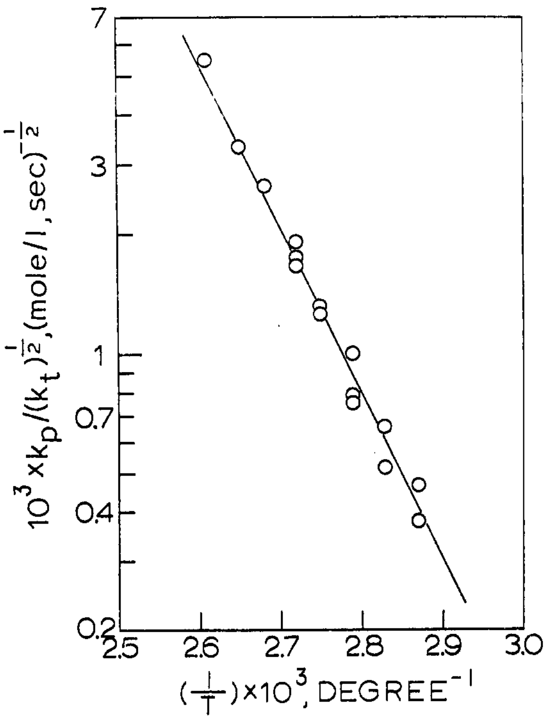

Figure 9. Values of $k_pk_t^{-1/2}$ as a function of T^{-1} for oxidation of PB.

Table XI
Rate Constants of Benzoyl Peroxide Initiated Autoxidation of Poly(1-butene)[a]

Temp, °C	$[PO_2] \times 10^6$, M	k_p, $(M\ sec)^{-1}$	$k_t \times 10^{-6}$, $(M\ sec)^{-1}$
90[b]	1.54	1.81	1.93
	1.58	1.83	2.00
	1.62	1.80	1.91
	1.68	1.73	1.77
	Av. 1.61 ± 0.06	1.79 ± 0.04	1.90 ± 0.1
95[c]	3.88	2.24	1.55
	3.52	2.47	1.89
	3.46	2.52	1.96
	Av. 3.62 ± 0.23	2.41 ±0.15	1.80 ± 0.22
100[d]	5.30	3.51	1.76
	4.76	3.90	2.19
	5.38	3.45	1.71
	5.66	3.28	1.55
	Av. 5.28 ± 0.38	3.54 ± 0.26	1.80 ± 0.27
105[e]	7.50	4.61	1.95
	8.24	4.19	1.62
	6.98	4.95	2.25
	7.76	4.45	1.82
	Av. 7.62 ± 0.56	4.55 ± 0.32	1.91 ± 0.31

[a] PO_2 = 1 atm. [b] $[BP]_0 = 0.5\ M$, $\alpha = 0.05$, $k_d = 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 1.3 \times 10^{-3}\ (M\ sec)^{-1/2}$. [c] $[BP]_0 = 0.5\ M$, $\alpha = 0.13$, $k_d = 1.8 \times 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 1.7 \times 10^{-3}\ (M\ sec)^{-1/2}$. [d] $[BP]_0 = 0.25\ M$, $\alpha = 0.3$, $k_d = 3.3 \times 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 2.64 \times 10^{-3}\ (M\ sec)^{-1/2}$. [e] $[BP]_0 = 0.25\ M$, $\alpha = 0.43$, $k_d = 5.1 \times 10^{-4}\ sec^{-1}$, $k_pk_t^{-1/2} = 3.3 \times 10^{-3}\ (M\ sec)^{-1/2}$.

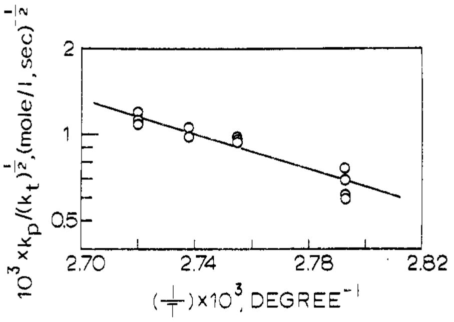

Figure 10. Values of $k_pk_t^{-1/2}$ as a function of T^{-1} for oxidation of PMP.

molecules with loops or traverses between several points of attachment on the fold surface.[74] In the case of crystallites in semicrystalline polymers, there are in addition tie molecules which have ends and segments incorporated in the crystallites. One may consider all these types of amorphous segments or molecules as "encumbered," whereas the remaining molecules of the amorphous phase can be said to be "free" in the sense that it is the same as that for a completely amorphous polymer.

The radicals of the "free" polymer molecules can diffuse apart or recombine with a probability more or less like molecules in liquids except for the greatly increased viscosity in polymer. The radicals formed in the reaction with the cilia, loops, tie molecules, or physically adsorbed amorphous segments are "encumbered." They can recombine with much higher probability than the radicals of the free polymer molecules. If in the first approximation all the "encumbered" radicals recombine and are scavenged by the added inhibitor molecules, then one can estimate the approximate fraction of amorphous molecules which are "encumbered." Comparison of the results in Tables III and IV suggests that this is as much as 90% for c-PB below 80°. At temperatures above 90°, this fraction decreases rapidly; it is only 30% at 105°. Of course there are no "encumbered" molecules above the melting point of the polymer.

The value of α represents the ratio of the rate constants $k_{diff}/(k_{cage} + k_{diff})$ where k_{cage} is for cage combination and k_{diff} is that of diffusion. Then $\alpha/(1 - \alpha)$ is simply k_{diff}/k_{cage}. An Arrhenius plot of $\alpha/(1 - \alpha)$ vs. T^{-1} should be linear with a slope of $E_{diff} - E_{cage}$ (Figure 11) which is found to be 21.8 kcal mol^{-1}. Three kinds of diffusion may be considered. The diffusion of inhibitor molecules has high activation energies; in polypropylene it is about 20 kcal mol^{-1} for didodecyl-3,3′-dithiodipropionate, *N*-octadecyldiethanolamine, and 1,1,3-tri(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane,[78] and about 34 kcal mol^{-1} for 2,4-dihydroxybenzophenone.[79] The activation energy for segmental dif-

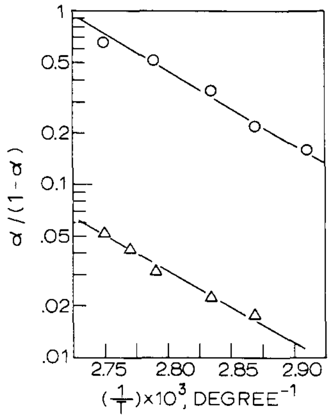

Figure 11. Variation of $\alpha/(1-\alpha)$ with T^{-1} for BP: (○) in a-PP; (△) in c-PB.

fusion of poly(propylene)[80] is about 10 kcal mol^{-1}. Third, diffusion can also result from propagation of radical by hydrogen abstraction; depending upon the reactivity of the radicals and the hydrogen being abstracted the activation energy can range from 9 to 16 kcal mol^{-1}. For cage combination the activation energy is negligible for R· + R·, R· + RO_2·, or RO_2· + RO_2·, in the third case only one of the RO_2 radicals can be tertiary. On the other hand if both RO_2 radicals are tertiary, the activation energy is about 7–13 kcal mol^{-1}.[6,33,84,85] The value of $E_{diff} - E_{cage}$ = 21.8 kcal mol^{-1} is most consistent to the requirement of diffusion of the AH molecule to scavenge the radicals.

Rate Constants of Autoxidation. A. Polypropylene. The values of $k_p k_t^{-1/2}$ obtained for self-initiated autoxidation[32] (110–140°) and those obtained here (71–105°) lie on the same curve (Figure 8) with the possible exception of the 140° results. The 45° result of Niki et al.[33] also seems to fit the plot. Buchachenko et al.[7] measured individual values of k_p and k_t for 2,4,6-trimethylheptane between 40.5 and 78.3°. Mill and Montorsi[6] reported $k_p k_t^{-1/2}$ for 2,4-dimethylpentane at 50, 100, and 125°. Since these are all model compounds for PP, the results are also shown in Figure 8. The agreement, based on tertiary hydrogens (as these are much more reactive than secondary or primary), is again quite good and suggests that autoxidations of amorphous polymer and liquid hydrocarbons resemble each other closely.

The values of k_p are shown in the Arrhenius plot (Figure 12). The results of Buchachenko et al.[7] also lie on the same curve: $k_p = 1.61 \times 10^7 \exp(-12080/RT)$ $(M\ \sec)^{-1}$. In Figure 12, the data at 140° seem definitely out of line. Possibly oxygen starvation becomes significant and there is rate limiting at this temperature. The value of k_p at 45° for a-PP reported by Niki et al.[33] is an order of magnitude smaller than that found by Buchachenko et al.[7] and that extrapolated from our data. The difference is due directly to the much higher concentration of PO_2 radicals observed by these workers. Mill and Montorsi[6] gave $k_p = 0.23$ $(M\ \sec)^{-1}$ per hydrogen at 100°. If we assume only tertiary hydrogens are oxidized, a value of $k_p = 1.84$ $(M\ \sec)^{-1}$ is obtained which lies not far from the line in Figure 12.

In our earlier work,[32] the values of k_t seemed to be temperature dependent. With the additional data of this work, it can be seen from the Arrhenius plot (Figure 13) that the 140° data were way off and that the termination process is temperature dependent. Not taking that into the plot we obtain for polypropylene $k_t = 1.11 \times 10^{13} \exp(-11600/RT)$ $(M\ \sec)^{-1}$. Buckachenko et al.[7] reported that k_t for oxidation of 2,4,6-trimethylheptane is temperature independent. Their results are shown as the horizontal bar in Figure 13.

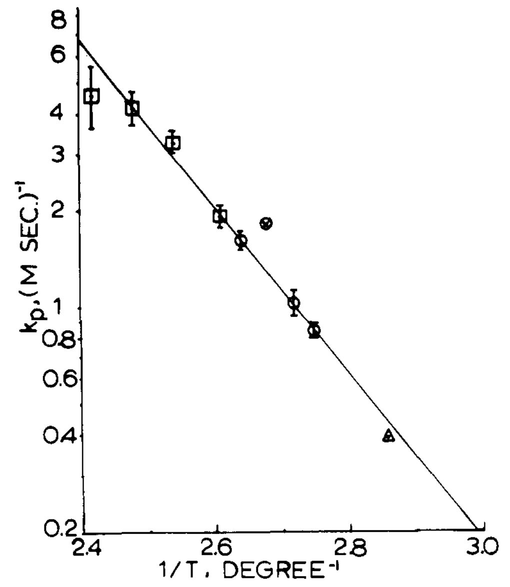

Figure 12. Arrhenius plot for the rate constant of propagation for oxidations of polypropylenes and model compounds: (○) a-PP (this work); (□) c-PP (ref 32); (⊗) 2,4-dimethylpentane (ref 6); (△) 2,4,6-trimethylheptane (ref 7).

Niki et al.[33] cited a value of $k_t = 5.1 \times 10^4$ $(M\ \sec)^{-1}$ for 2,4-dimethylpentane at 45° in their Table X. Extrapolation of the line in Figure 13 to 45° gave a value of 1.2×10^5 $(M\ \sec)^{-1}$, a factor of 2 in difference.

The value of k_t for a-PP arrived at by Niki et al.[33] is only 23 $(M\ \sec)^{-1}$ which is 5000-fold smaller than that extrapolated from our results. The reason lies in the very high concentration of PO_2 radicals detected by these authors, higher than ours by about two orders of magnitude. Since k_t is proportional to $[PO_2]^{2-}$, the differences in k_t can be understood. Even though it is very difficult to obtain accurate measures of radical concentration by ESR for the kind of samples used in these works, a difference of two orders of magnitude seems unlikely. More measurements are definitely needed to resolve the difference.

B. Poly(1-butene). From the values of $k_p k_t^{-1/2}$ given in Table VII and the radical concentrations, the results of k_p and k_t are summarized in Table XI. Because of the limited temperature range the data encompasses, an Arrhenius

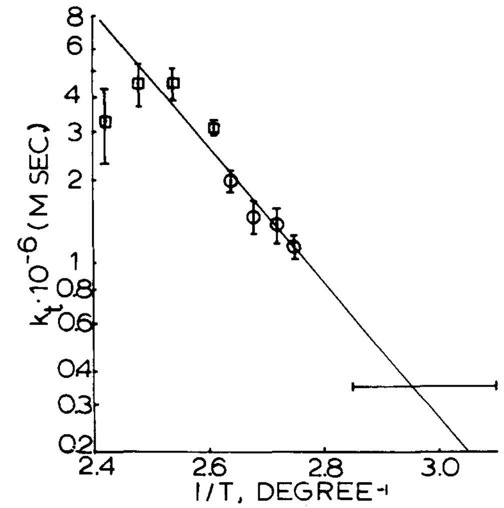

Figure 13. Arrhenius plot for the rate constant of termination for oxidations of polypropylenes: (○) a-PP initiated by BP (this work); (□) c-PP self-initiated (ref 32); (⊢⊣) a-PP initiated by di-*tert*-butyl peroxyoxalate (ref 33).

plot is not justified. However, we note the following comparisons with PP. The values of k_p for PB are two to three times greater than those for PP. There is also a greater temperature dependence; the activation energy for propagation is approximately 18 kcal mol^{-1}. The limited data showed almost no temperature dependence for k_t. However, more data over a wider temperature range are needed before a firm statement can be made about the activation energy of termination for PB.

C. Poly(4-methyl-1-pentene). No ESR measurements were made on this polymer. Comparison of the values of $k_pk_t^{-1/2}$ for PP and PMP given in Tables VI and VIII showed that they agree well within the experimental accuracy of 10%. This seems to support the assumption that both the crystalline and the amorphous phase of PMP undergo autoxidation.

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