[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

Radical Polymerization of 2,6-Dimethyl-4-*t*-butylstyrene[1]

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Polymerizations of the sterically hindered 2,6-dimethyl-4-*t*-butylstyrene initiated with heat, ultraviolet light and di-*t*-butyl peroxide gave normal addition-type polymers of moderate molecular weight (1800–7700). Results of rate experiments at several temperatures and the effect of conversion, initiator and temperature on polymer molecular weights, coupled with information on initiator efficiency and polymer unsaturation, show that the mechanism of polymerization of 2,6-dimethyl-4-*t*-butylstyrene differs from those of less hindered styrenes. These differences are mainly the absence of the usual bimolecular radical termination reaction and the prominence of chain transfer with monomer, both in the usual sense and as "degradative chain transfer" in which the kinetic chain is terminated by transfer of hydrogen atoms from monomer to polymer radicals, leaving unreactive monomer radicals incapable of initiating further polymerization.

The literature shows that the sterically hindered 2,6-dimethyl substituted styrenes are resistant to polymerization by radical processes. Thus, it has been reported that: (i) 2,6-dimethylstyrene gave 25% of an oily polymer when heated at 184° for 48 hr.[2]; (ii) 2,4,6-trimethylstyrene yielded a polymer with a molecular weight of 2800 after 40 hr. at 190°[3] and 8% conversion to a very low polymer (mol. wt. 550) on heating with 5% benzoyl peroxide at 100°[4]; (iii) 2,6-dimethyl-4-*t*-butylstyrene was unaffected by exposure to direct sunlight and by heating with benzoyl peroxide, but it was polymerized to a "very low molecular weight" product by heating at 200° for 200 hr.[5] Therefore, when our exploratory experiments showed that 2,6-dimethyl-4-*t*-butylstyrene can be polymerized readily by di-*t*-butyl peroxide and by ultraviolet light, further study of the radical polymerization of this monomer was undertaken.

Results and Discussion

Polymerizations of 2,6-dimethyl-4-*t*-butylstyrene (DMBS) were initiated with heat, with ultraviolet light, and with di-*t*-butyl peroxide. A comparison of peroxide and thermally initiated polymerizations using an identical time–temperature sequence is shown in Table I. Polymerization data and properties of polymers obtained from di-*t*-butyl peroxide and ultraviolet light initiated experiments at fixed temperatures are summarized in Tables II and III. Di-*t*-butyl peroxide concentrations listed in Table II were not measured directly, but, because the rate of decomposition of this initiator at a given temperature is essentially independent of environment,[6,7] these values were calculated from decomposition rates in *t*-butylbenzene.[8] The polymers obtained were shown by spectrographic studies to be normal addition-type polymers; their molecular weights were estimated as 1800–7700 from intrinsic viscosity measurements. The effects of conversion, temperature and initiator on degree of polymerization are summarized graphically in Fig. 1.

TABLE I

COMPARATIVE DI-*t*-BUTYL PEROXIDE AND THERMALLY INITIATED POLYMERIZATIONS OF 2,6-DIMETHYL-4-*t*-BUTYLSTYRENE

Initiator	$(t\text{-BuO}_2)_2$, 0.5 wt. %	Heat
Reaction time and temp.,[a] hr. (°C.)	24(95), 7(120) 7(175), 7(210)	24(95), 7(120) 7(175), 7(210)
Appearance of total product	Soft, sl. sticky, colorless solid	Colorless, mobile liq.
MeOH pptd. polymer, wt. %	61	8.4
Intrinsic vis. [η], 100 ml./g.	0.145	0.095
Temp., °C.	27.8	37.7
Solvent	Toluene	Benzene
Mol. wt.	5300	3500

[a] The samples were heated successively at the indicated temperatures for the periods shown.

Mechanism.—This study is not complete enough to provide an unambiguous detailed mechanism for the radical initiated polymerization of DMBS. However, differences between this and more usual vinyl polymerizations can be clearly seen by consideration of the following facts and plausible alternative mechanisms devised which are consistant with these observations.

A. Percentages of monomer polymerized at three temperatures plotted against the amounts of di-*t*-butyl peroxide decomposed are shown in Fig. 2. These curves show that at each temperature dM/dP[9] is very nearly constant until more than half of the monomer has disappeared. The ratios then increase gradually until discontinuities in the curves are reached due to solidification of the polymerization samples. Polymerization continues in the solids but at very much lower initiator efficiencies.

B. Chain transfer initiating further polymerization is important with DMBS. Values of dM/dP listed in Table IV show that the moles of monomer polymerized per mole of peroxide decomposed decrease from 356 to 140 as the temperature is raised from 110 to 145°. If all radicals resulting from

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[1] Presented before the Petroleum Division of the American Chemical Society, Cincinnati, Ohio, April 6, 1955; "General Papers," Publication No. 33, Division of Petroleum Chemistry, p. 193.

[2] M. G. Sturrock and T. Lawe, U. S. Patent 2,555,298 (May 29, 1951).

[3] G. T. Kennedy and F. Morton, *J. Chem. Soc.*, 2383 (1949).

[4] A. de Pauw and G. Smets, *Bull. soc. chim. Belges*, **59**, 629 (1950).

[5] (a) V. V. Korshak and N. G. Matveeva, *Doklady Akad. Nauk S.S.S.R.*, **78**, 1145 (1951); (b) V. V. Korshak and N. G. Matveeva, *Zhur. Obshcheĭ Khim.*, **22**, 1173 (1952).

[6] F. H. Dickey, J. H. Riley, F. F. Rust, R. S. Treseder and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

[7] (a) J. Murawski, J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, **19**, 698 (1951); (b) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948).

[8] Values for the first-order rate constants for the decomposition of di-*t*-butyl peroxide estimated from the data of Dickey, *et al.*,[6] are: 0.31×10^{-5} sec.$^{-1}$ (110°), 1.5×10^{-5} sec.$^{-1}$ (125°), 15×10^{-5} sec.$^{-1}$ (145°).

[9] The symbols M and P used throughout this paper refer to moles of monomer and moles of di-*t*-butyl peroxide, respectively.

TABLE II

POLYMERIZATION OF 2,6-DIMETHYL-4-*t*-BUTYLSTYRENE INITIATED WITH DI-*t*-BUTYL PEROXIDE (0.5 WT. %)

Time °C.	Time, hr.	Appearance of total product[a] At reacn. temp.	After cooling	MeOH pptd. polymer wt. %	Unreacted monomer u.v. anal. wt. %	Total wt. %	Unreacted (t-BuO$_2$)$_2$, wt. %	Intrinsic vis. at 25°, 100 ml./g.	Mol. wt.	Capillary m.p.'s,[b] °C. Sinter point	Melting range
110	8	Mobile liq.	Sl. viscous liq.	20.0	80.5	100.5	0.454	0.190	7000	225	250–257
	24.5	Viscous liq.	Semi-solid	54.6	44.5	99.1	.383	.205	7500	220	243–258
	48	Glass	Brittle, fractured resin	89.7	9.5	99.2	.294	.210	7700	213	240–256
125	3	Mobile liq.	Sl. viscous, liq.	26.0	74.7	100.7	.425	.160	5900	236	254–262
	6	Viscous liq.	Very viscous, liq.	46.5	52.0	98.5	.361	.165	6100	215	244–256
	12	Glass	Brittle, fractured resin	90.0	9.0	99.0	.261	.180	6600	215	246–256
	24	Glass	Brittle, fractured resin	93.0	5.5	98.5	.137	.175	6400	215	244–256
	48	Glass	Brittle, fractured resin	93.8	4.0	97.8	.037	.170	6300	220	241–255
145	1	Mobile liq.	Viscous liq.	37.5	59.3	96.8	.293	.120	4400	221	238–254
	2	Viscous liq.	Very viscous liq.	61.0	37.8	98.8	.172	.130	4800	217	242–258
	4	Glass	Brittle, fractured resin	94.6	4.0	98.6	.059	.140	5200	217	236–256
	8	Glass	Brittle, fractured resin	95.3	3.0	98.3	.007	.140	5200	209	241–254

[a] Products were all colorless or very pale yellow. [b] Sinter point is the first detectable change in a powdered sample. The melting range begins at the temperature at which the particles of white powder partially coalesce giving a colorless solid and ends when all of this solid has melted.

TABLE III

ULTRAVIOLET INITIATED POLYMERIZATION OF 2,6-DIMETHYL-4-*t*-BUTYLSTYRENE

Temp., °C.	Time, hr.	U.v. radiation factor[a]	MeOH pptd. polymer, wt. %	Unreacted monomer, u.v. anal. wt. %	Total wt. %	Intrinsic vis. at 25°, 100 ml./g.	Mol. wt.	Capillary m.p.'s[b], °C. Sinter point	Melting range
25[c]	209	Approx. 1	33	...	...	0.05[d]	1800	...	...
150	2.92	1	5.9	94.5	100.4	.140	5200	225	245–252
	4.67	1	9.5	90.5	100.0	.140	5200	230	245–251
	13.92[e]	1	26.2	71.5	97.7	.140	5200	225	232–253
180	2.75	0.90–0.95	12.8	...	...	...	...	...	...
	5.0	0.90–0.95	21.1	75.0	96.1	.115	4200	219	236–250

[a] Amount of radiation absorbed by 1 g. of sample per unit time divided by amount absorbed at 150°. [b] See footnote *b*, Table II. [c] Air was not excluded during this experiment. [d] Relative viscosities were measured at 37.7°. [e] The area of the ultraviolet source which was immersed in the mixture decreased 8% during this period due to contraction resulting from polymerization and evaporation of monomer.

the decomposition of the peroxide initiate polymerization, two chains are initiated for each molecule reacted, and $(\mathrm{d}M/\mathrm{d}P)/2$ is the kinetic chain length for the reaction. Dividing this by the average degree of polymerization ($\overline{DP}$) gives the number of polymer chains resulting from one initiator radical. These figures are shown on the last line of Table IV. Since not more than one of these chains can be initiated by a radical from the peroxide, the remaining 2.0 to 3.7 chains must be started by radicals resulting from chain transfer to monomer. If the efficiency factor of the initiator is less than one, active chain transfer must play an even larger role.

TABLE IV

CONSTANTS FOR THE POLYMERIZATION OF 2,6-DIMETHYL-4-*t*-BUTYLSTYRENE INITIATED WITH DI-*t*-BUTYL PEROXIDE (0.5 WT. %)

Temp., °C.	110	125	145
$\mathrm{d}M/\mathrm{d}P$	356	266	140
$\overline{DP}$	38	31	23
$(\mathrm{d}M/\mathrm{d}P)/2\overline{DP}$	4.7	4.3	3.0

C. The average degree of polymerization ($\overline{DP}$) was found to increase from 15–25% as the monomer conversion was increased from 0 to 90%. This is shown graphically in Fig. 1.

In general terms, the principal mechanism of the di-*t*-butyl peroxide initiated polymerization of

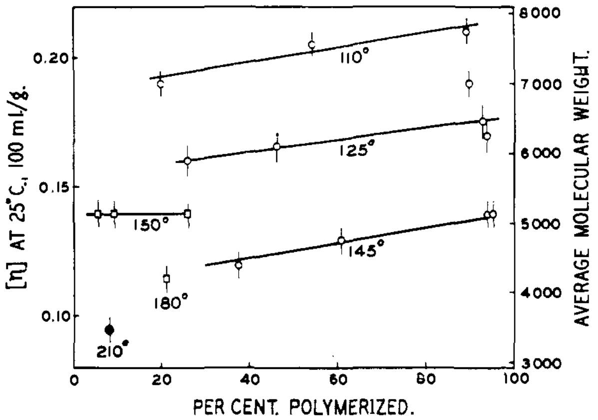


Fig. 1.—The effect of conversion, temperature, and initiator on the degree of polymerization of 2,6-dimethyl-4-*t*-butylstyrene: initiator: ○, 0.5 wt. % di-*t*-butyl peroxide; □, ultraviolet light; ●, heat.

DMBS can probably be represented by some combination of the following steps

$$\text{Initiation} \qquad \mathrm{P} \xrightarrow{k_1} 2\mathrm{R}\cdot \tag{1}$$

$$\text{Propagation:} \qquad \mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} + \mathrm{R}\cdot \tag{2}$$

$$\text{Chain transfer:} \qquad \mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{tr}} \mathrm{RH} + \mathrm{R}\cdot \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{t}} \mathrm{RH} + \mathrm{M}\cdot \tag{4}$$

$$\mathrm{M}\cdot \xrightarrow{k_r} \mathrm{R}\cdot \qquad (5)$$

Termination:

$$2\mathrm{R}\cdot \xrightarrow{k_T} \mathrm{RR\ or\ RH} + \mathrm{R'CH{=\!=}CH_2} \qquad (6)$$

$$2\mathrm{M}\cdot \xrightarrow{k_z} \mathrm{MM} \qquad (7)$$

In these expressions P represents di-*t*-butyl peroxide, M is monomer, R· is any radical capable of adding to monomer and M· represents radicals which do not add to monomer. In the derivation of the equations which follow, it was assumed that the efficiency, *f*, of the initiator is constant at a given temperature and that the radicals formed in 1, 2, 3 and 5 behave identically.

The usual type of peroxide-initiated polymerization of vinyl monomers involving chain transfer with monomer and termination by bimolecular radical combinations or disproportionations consists of steps 1, 2, 3 and 6. This leads to expressions of the types

$$\log M = KP^{1/2} + C \qquad (8)$$

$$\frac{1}{\overline{DP}} = K' + K'' P^{1/2}M^{-1} \qquad (9)$$

This mechanism was ruled out for DMBS because the plot of log M against $P^{1/2}$ was far from the linear relation required by eq. 8. Also, the polymerization data show that $P^{1/2}M^{-1}$ increases with conversion and, therefore, the degree of polymerization ($\overline{DP}$) should decrease. Actually a small increase was observed.

The nearly constant dM/dP observed with DMBS and previously with 2,4,6-trimethylstyrene[4] suggests a polymerization terminated by "degradative chain transfer"[10] as an attractive alternative. This consists of steps 1, 2, 3, 4 and 7 and gives the expressions

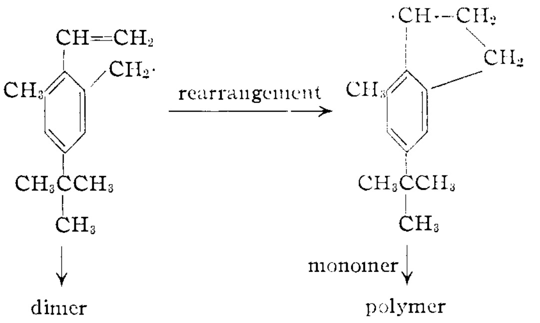
$$\mathrm{d}M/\mathrm{d}P = \frac{2f(k_p + k_{tr} + k_t)}{k_t} \qquad (10)$$

$$DP = \frac{k_p}{k_{tr} + k_t} \qquad (11)$$

In the benzoyl peroxide-induced polymerization of allyl acetate, Bartlett and Altschul[10] found that dM/dP was constant in any given run but that it decreased from 28.8 to 15.6 as the initial benzoyl peroxide concentration was increased from 1.01 to 9.95 weight per cent. The degree of polymerization did not change significantly. They concluded that wastage of benzoate radicals by interaction occurred and that this was greater at higher benzoyl peroxide concentrations. As only one initiator concentration was used in the experiments reported here, it is not known with certainty whether the di-*t*-butyl peroxide initiated polymerization of DMBS is analogous in this respect. Further experiments using other initiator concentrations should be run. If such reactions do occur here, the efficiency factor *f* shown in eq. 10 is not constant but increases with decrease in initiator concentration. An increase in dM/dP is, in fact, noticeable at high conversions in the curves shown in Fig. 2. However, the low initial peroxide concentration used (0.5 weight per cent.) should minimize this effect. Equation 11 predicts that for this mechanism the degree of polymerization should be independent of monomer and peroxide concentrations. The small increase observed with increasing conversion could result from further reactions involving the increasing proportion of polymer molecules in the reaction mixture.

Transfer reactions play an important part in this polymerization. With the mechanisms under consideration, which have not been ruled out, every polymer molecule results from reaction of a polymer radical with monomer. Chain transfer occurs if the new radicals which are formed initiate further polymerization; "degradative chain transfer" occurs if they do not. The most plausible transfer reactions are removal by the polymer radical of hydrogen atoms from the monomer at (a) the two *o*-methyl groups, (b) the *p*-*t*-butyl group or (c) the vinyl group. The benzyl radical resulting from (a) is stabilized by 15–20 kcal. of benzyl resonance and also by resonance with the vinyl group. It is probable that unreactive radicals of this kind terminate the kinetic chain and constitute the "degradative chain transfer." Radicals resulting from (b) or (c) would be more reactive and might be expected to be responsible for chain transfer. However, addition of the unrearranged radicals from (b) or (c) to monomer should give product in which more than 75% of the total polymer molecules contain an aliphatic double bond. Instead, spectrographic analysis of polymer from di-*t*-butyl peroxide initiated polymerizations showed positively that not more than 20%, and probably less than 5%, of the polymer chains contained an aliphatic double bond.

One explanation is possible if it is assumed that the neophyl radical resulting from (b) rearranges in known manner[11] to a tertiary radical which then transfers a hydrogen atom to monomer. The resulting monomer radical would not contain an aliphatic double bond and would initiate further polymerization. A more attractive alternative is internal rearrangement of the benzyl radical from (a) to give a radical capable of initiating further polymerization.[12]



This mechanism consists of steps 1, 2, 4, 5 and 7 and gives the equations

$$\mathrm{d}M/\mathrm{d}P = \frac{(k_p + k_t)}{k_t}\left[2 + \frac{k_r}{(fk_ik_z)^{1/2}P^{1/2}}\right] \qquad (12)$$

$$\overline{DP} = k_p/k_t \qquad (13)$$

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[10] P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 816 (1945).

[11] (a) W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944); (b) S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

[12] We are indebted to a referee for this suggestion.

Equation 12 predicts that decreasing the peroxide concentration should increase dM/dP. Under the conditions used, this effect could be quite small and might very well result in approximations of the curves shown in Fig. 2. This mechanism and "degradative chain transfer" both predict that the degree of polymerization should be constant.

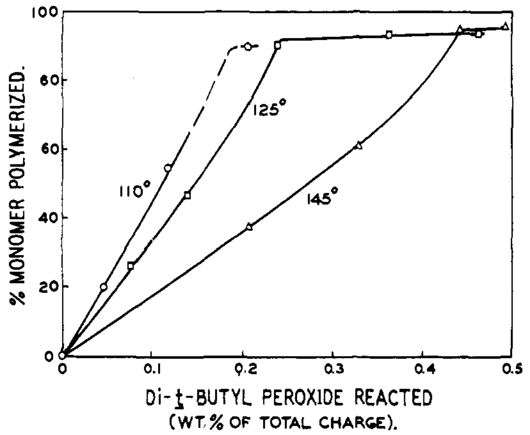

Fig. 2.—Di-*t*-butyl peroxide (0.5 wt. %) catalyzed polymerization of 2,6-dimethyl-4-*t*-butylstyrene.

The thermal and ultraviolet light initiated polymerizations are probably similar to that of the di-*t*-butyl peroxide induced polymerization except for the initiation steps.

Effect of Temperature on Chain Transfer and Initiator Efficiency.—The data from Table III plotted in Fig. 3 show that an increase in the rate of the ultraviolet light initiated polymerization of DMBS occurred when the temperature was raised from 150 to 180°. That this increase was not caused by a change in the emitted radiation of the ultraviolet source was established by studying its temperature characteristics. This showed that actually 5–10% less radiation was obtained at 180° compared to that obtained at 150°. The possibility that the temperature coefficient of the polymerization rate was due to thermal initiation superimposed on photochemical initiation was also considered. However, even though the thermal rate at 180° is assumed to be as high as that observed at 210° and is assumed as zero at 150°, the residual rate of polymerization at 180° due to ultraviolet light initiated polymerization is still more than 1.6 times as high as the rate at 150°. Therefore the observed increase in rate must result largely from the effect of temperature on the polymerization reaction sequence initiated by absorbed ultraviolet light.

The efficiency of ultraviolet light in initiating polymerization is probably nearly the same at 150 and 180°. However, the polymerization rate is increased and the molecular weight of the polymer is decreased by raising the temperature. Therefore, propagation rate is increased relative to the termination reactions and the ratio of active chain transfer to reactions terminating the kinetic chain is increased.

If this is also the case with the di-*t*-butyl peroxide initiated polymerization, then here, too, the proportion of the total polymer formed by polymerization initiated by chain transfer must increase with temperature. However, from the last line in Table IV it is seen that while 4.7 polymer molecules are formed at 110° for every radical theoretically available from the initiator, only 3.0 molecules are obtained at 145°. Therefore, it appears that di-*t*-butyl peroxide is more than twice as efficient in initiating the polymerization of DMBS at 110° than it is at 145°. It is probable that the addition of the *t*-butoxy radical to the monomer is comparatively slow, compared to less hindered styrene monomers, because of a lower frequency factor and a somewhat higher activation energy resulting from steric inhibition of resonance. Competing with the vinyl group for these radicals are the reactive hydrogen atoms on the alkyl groups and the thermal decomposition of *t*-butoxy radicals, which give acetone and reactive methyl radicals. It is known that the decomposition of the *t*-butoxy radical has a higher temperature coefficient than reaction of the *t*-butoxy radical with cumene,[6] and it is probable that the reactions competing with addition of the *t*-butoxy radical to the double bond of the monomer become relatively more important as the temperature is raised. While some of the methyl radicals may initiate polymerization, they are more reactive and, therefore, less selective than the *t*-butoxy radical so that a larger percentage probably is wasted.

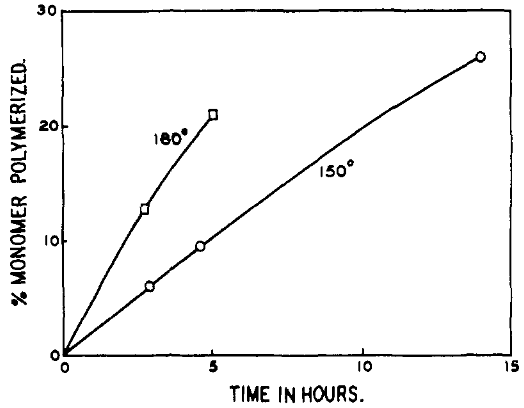

Fig. 3.—Ultraviolet light initiated polymerization of 2,6-dimethyl-4-*t*-butylstyrene.

Effect of Initiator on Polymer Molecular Weight.—The effects of temperature and initiator on polymer molecular weight are shown in Fig. 1. Higher temperatures result in higher polymer molecular weights, but at the same temperature higher polymers are obtained on initiation with ultraviolet light rather than di-*t*-butyl peroxide. The latter effect may be the result of biradical formation by irradiation of DMBS. If the two ends of the biradicals behave independently, the polymer molecules initiated by these would grow to twice the size of the higher proportion of polymer molecules initiated in the same environment by chain transfer. While growing polymer biradicals ordinarily are believed to terminate at an early stage of their growth by cyclization or intramolecular disproportionation, with DMBS these processes are effectively inhibited by steric hindrance.

Table I shows that thermal polymerization of DMBS gave lower molecular weight polymer than was obtained by di-*t*-butyl peroxide initiation using an identical time–temperature reaction sequence. This resulted because most of the thermal polymerization occurred at 210° while most of the di-*t*-butyl peroxide initiated polymerization occurred at 120° and while heating from 120–175°. At this point most of the peroxide had been decomposed.

Experimental

2,6-Dimethyl-4-*t*-butylstyrene was prepared as previously described.[13] All samples used were freshly distilled and reasonable care taken to exclude air from contact with monomer and to avoid contamination of distillate fractions with stopcock grease.

Di-*t*-butyl Peroxide Catalyzed Polymerizations.—These were all carried out on approximately 3-g. samples contained in evacuated Pyrex ampoules. The contents of the ampoules were degassed by alternately freezing and melting at 1 mm. pressure until no more bubbles were given off. The ampoules were also flushed with high purity nitrogen (99.99%) several times during this process. The samples used in the rate experiments (Table II) were aliquots of a thoroughly mixed solution of 0.165 g. (0.5 wt. %) redistilled di-*t*-butyl peroxide[14] in 33.00 g. of DMBS. The samples were heated in an oil-bath regulated to ±0.2°. They were examined visually just before removing from the bath and again after cooling.

Thermal Polymerization.—A 3-g. sample of monomer without added di-*t*-butyl peroxide (Table I) was treated in exactly the same manner as a sample containing 0.5 weight per cent. of di-*t*-butyl peroxide.

Ultraviolet Light Initiated Polymerizations.—The polymerization at 25° (Table III) was carried out by irradiating 2.69 g. of DMBS with a 10-watt quartz–mercury arc by immersing 23% of the radiating surface of the pencil source directly in the monomer contained in a small test-tube. Temperature was controlled by immersing the tube in a thermostat; no effort was made to exclude air.

The experiments at 150 and 180° summarized in Table III were carried out with the same ultraviolet light source using 3-g. samples of monomer at 150°, 2.90 g. at 180°. The Pyrex reaction tube had a 1.2 mm. clearance around the quartz–mercury arc. It was constricted to fit closely around the tube above the sample level. A side tube was provided above the constriction. The samples were weighed into the reaction tube before inserting the quartz–mercury arc. The tube was capped and the monomer degassed by alternately freezing, melting and flushing with nitrogen, as described for the di-*t*-butyl peroxide catalyzed polymerizations. The cap was then removed while maintaining a good flow of nitrogen through the side arm and the quartz–mercury arc immediately inserted. The reaction tube was immersed in a thermostat, controlled to ±0.2°; a slow stream of high purity nitrogen was maintained through the side arm and when the sample reached the temperature of the bath it was irradiated for the desired time. A constant voltage to the mercury arc was maintained with a constant voltage transformer. About 72% of the radiating surface of the arc was immersed in the monomer. The 1.2-mm. path of light through monomer contained in the cell was sufficient to absorb all of the radiation from the arc below a wave length of 3000 Å. at the maximum conversion attained in any experiment. The amount of light absorbed decreased slightly during the course of the reaction because polymerization and evaporation of monomer caused contraction of the sample, thereby reducing the area of the surface of the quartz–mercury arc immersed in the reaction mixture. These contractions were variable and were not accurately determined. If corrections were applied, the curves in Fig. 3 would approximate straight lines.

The radiation from the ultraviolet source was investigated, using a Cary model-11 ultraviolet spectrometer. This showed that most of the emitted radiation occurred at the 2537 Å. mercury resonance line, with a minor proportion at 2967 and 3126 Å. The lamp was found to have a high temperature coefficient, the radiation dropping about two-thirds in intensity as the temperature was raised from 70 to 150°. Inspection of the spectra at 150 and 180° indicated that the intensity of the 2537 Å. line gives an approximate idea of the relative amount of radiation at the two temperatures. The spectra were recorded in duplicate using a wide slit (2 mm.) and peak heights taken as a measure of relative intensity. While the Cary instrument is not well adapted for this type of measurement, the results do show definitely that the intensity is less at 180 than at 150° and that this difference is approximately 5–10%.

Analysis of the Reaction Products.—The percentage conversion of monomer to polymer in each experiment was determined from the weight of polymer precipitated on adding 1.5 liters of methanol to 2 g. of the total product dissolved in 60 ml. of benzene. The ASTM 703-44T procedure for methanol-insoluble content of polystyrene[15] was followed, but on four times the scale described. Unreacted monomer was determined by ultraviolet spectrographic analysis of solutions of samples of the total products in purified dioxane, calibrating against standard solutions of pure monomer and precipitated polymer from a 12-hr. di-*t*-butyl peroxide initiated polymerization at 125° (Table II). At a concentration of 1 g./l. and wave length of 2540 Å., the polymer had an absorbance of 0.479 unit as compared with an absorbance of 51.13 units for the monomer. Small corrections for the absorption of unreacted di-*t*-butyl peroxide were made where applicable. The sums of the weight percentages of methanol precipitated polymer and unreacted monomer fell between 96.1 and 100.7%.

Viscosities and Molecular Weights of Polymers.—Intrinsic viscosities of similar polymers are approximately proportional to their molecular weights. Relative viscosities of the methanol precipitated polymers obtained in the experiments summarized in Tables II and III were determined at 25° for 0.5, 1 and 2% solutions in benzene. The viscosities were determined in duplicate using Zeitfuchs viscometers[16] having solvent times of 80 and 130 seconds. Extrapolation of the inherent viscosities ($\ln \eta_r/C$) and the reduced viscosities (η_{sp}/C) to zero concentration gave the intrinsic viscosity $[\eta]$. The inherent viscosities showed very little change with concentration, but the reduced viscosities decreased rapidly with decreasing concentration. The solvents and temperatures used in determining the intrinsic viscosities of the polymers obtained in the preliminary experiments are shown in Table I. As intrinsic viscosity does not change greatly with solvent or temperature, these values can be compared directly with those reported in Tables II and III.

The molecular weights reported here are probably not very accurate, although they should provide as good an indication of the relative molecular weights of the polymers described as do the intrinsic viscosities from which they were derived. They were calculated for comparison with the molecular weights of other 2,6-disubstituted styrenes calculated in a similar manner by other investigators,[3,17] using the Kemp and Peters expression[18] in the manner described by Kennedy and Morton.[3] The cryoscopic molecular weight for the polymer of lowest molecular weight (Table III) was determined in benzene. Although the determination was close to the limit of sensitivity of the available equipment, it indicated that this polymer has a cryoscopic molecular weight higher than 2500. compared with 1800 obtained by the indicated calculation.

Spectrographic Studies.—The infrared and ultraviolet spectra of the methanol-insoluble polymer from the di-*t*-butyl peroxide initiated polymerization of DMBS (Table I) and for the monomer and its ethyl analog were recorded.[19] These were examined to see if spectra could be used in following the course of polymerization, whether the polymer was unsaturated and whether the spectra of the polymer were consistent with those expected for a product resulting from normal addition polymerization. From the infrared spectra, it is apparent that differences in absorption of the monomer and polymer at 6.15, 10.9 and 13.2μ are great enough to be useful in the analysis of monomer–polymer mixtures; but as a greater difference in absorption occurs in the ultraviolet spectrum at 2450 Å., the latter was used

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[13] M. J. Schlatter, THIS JOURNAL, **76**, 4952 (1954).

[14] Constant boiling, center cut product obtained by distilling commercial di-*t*-butyl peroxide (Shell Chemical Corp.) through a 15-plate column at 50 mm. pressure.

[15] R. H. Boundy and R. F. Boyer, Editors, "Styrene, Its Polymers, Copolymers and Derivatives," ACS Monograph No. 115, Reinhold Publishing Corp., New York, N. Y., 1952, p. 315.

[16] E. H. Zeitfuchs, *Proc. Am. Petroleum Inst.*, **20 III**, 104 (1939).

[17] C. S. Marvel, C. G. Overberger, R. E. Allen, H. W. Johnston, J. H. Saunders and J. D. Young, THIS JOURNAL, **68**, 861 (1946).

[18] A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

[19] These spectra have been deposited as Document number 4799 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm payable to Chief, Photoduplication Service, Library of Congress.

in determining unreacted monomer in the rate experiments summarized in Tables II and III. Estimation of the probable maximum unsaturation in the polymer is complicated by the fact that the minimum in the completely saturated polymer spectrum corresponding approximately to the monomer ultraviolet maximum is not a point of zero absorption but rather is a "valley" between absorption maxima. In the polymers investigated, this minimum was lower than the corresponding minimum in 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene, which suggests that there is a very little unsaturation in the polymer. This probably amounts to less than one double bond for every twenty polymer molecules. However, even if the total absorption of the polymer at 2450 Å. is attributed to unsaturation, the polymer contains only 0.8% of the original aliphatic double bonds of the monomer which still corresponds to only one double bond for every four polymer molecules (mol. wt. 5200).

The infrared spectra of the polymer and 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene should be very similar, if the polymer results from normal addition polymerization. Comparison of the two spectra shows that this is the case. All of the infrared absorption maxima in the spectrum of the polymer have their counterparts in the spectrum of 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene, with the exception of small peaks at 9.3 and 13.2μ. Absorption at 6.35, 6.9 and 13.4μ is considerably attenuated in the spectrum of the polymer compared to that of 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene; and peaks at 7.6, 9.15, 9.4, 10.35, 12.75 and 14.4μ in the spectrum of the latter are not in evidence in the polymer spectrum. The peak at 13.4μ and all of those listed in the second group are also absent in the spectra of the series of hydrocarbons in which the ethyl group of 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene is replaced by methyl, *n*-decyl and *n*-octadecyl[13]; but all have their counterparts in the spectrum of 1,3,5-trimethyl-2-ethylbenzene.[20] Therefore, their absence is to be expected in a normal addition-type polymer. The intense absorption at 11.5μ, which is present in the spectra of 2,6-dimethyl-4-*t*-butylstyrene, its polymer and its ethyl analog, is due to the vibration of the isolated nuclear hydrogens in the 4- and 6-positions in and out of the plane of the ring. Its presence indicates that the relationship of the alkyl groups on the nucleus and the structure of this part of the monomer molecule are unchanged by the polymerization.

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[CONTRIBUTION FROM THE FRUIT AND VEGETABLE CHEMISTRY LABORATORY, WESTERN UTILIZATION RESEARCH BRANCH, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Plant Polyphenols. I. The Polyphenolic Constituents of the Pellicle of the Walnut (*Juglans regia*)[1]

BY LEONARD JURD

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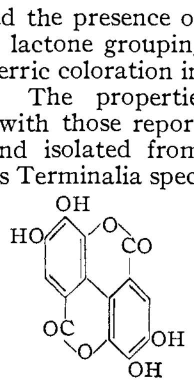
A study of the natural antioxidants in walnut pellicles has been undertaken. Ellagic acid, methyl gallate, gallic acid and a tannin were isolated from extracts of the pellicle. The tannin was composed chiefly of four polyphenolic esters or glucosides, and on hydrolysis gave ellagic acid, gallic acid, methyl gallate and glucose. Preferential oxidation of these pyrogallol derivatives in the pellicle probably aids in stabilizing walnut kernel constituents against decomposition.

In recent years it has become increasingly apparent that many naturally occurring polyphenolic compounds may function as antioxidants or be involved as substrates in the enzymic browning of plant tissues. Relatively few investigations into the nature of the natural phenolic substrates, however, have been reported,[2] although catechol compounds have been suggested as possible substrates and the reaction of polyphenol oxidases with such catechol derivatives as caffeic acid esters, catechins and flavonols has been proved.[3] In this Laboratory it has been observed that the oxidative deterioration of walnut kernels is inhibited by the presence of an intact pellicle (skin). It was of interest, therefore, to determine the nature of the compounds responsible for the protective properties of the pellicle. Previous work on walnuts has been limited to the isolation by Daglish[4] and others of an α-hydrojuglone glucoside from the leaves and pericarp. This was proved to be 1,5-dihydroxy-4-glucosidoxynaphthalene.[5] Bate-Smith[6] recently reported that an extract of the seed coat produced cyanidin when boiled with acids.

From the ether-soluble fraction of methanolic extracts of the pellicle a yellow crystalline phenol, $C_{14}H_6O_8$, was obtained. The reactions of this phenol indicated the presence of a 4,4′-dihydroxybiphenyl and a lactone grouping, and furthermore it gave a blue ferric coloration indicative of a pyrogallol nucleus. The properties of the phenol agreed closely with those reported for ellagic acid (I), a compound isolated from the ellagitannins found in various Terminalia species.[7]



I

Direct comparison of the spectra, R_f values, fluorescence and color reactions on paper chromatograms of

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[1] Presented at Meeting of Biological Chemistry Section, American Chemical Society, April, 1956, Dallas, Texas. Financial support for this work was provided by the California Walnut Growers Association.

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