Summary

1. The condensation of t-butyl chloride with cyclohexene in the presence of aluminum chloride at -25 to $-15°$ results in a 72% yield of chlorobutylcyclohexane, about 85% of which is 1-chloro-3-t-butylcyclohexane, the remainder being 1-chloro-t-butylcyclohexane.

2. The use of bismuth chloride as catalyst at $0°$ and at room temperature results in 5 and 21–25% yields, respectively, of similar mixtures of 1-chloro-3-t-butylcyclohexane with minor amounts of 1-chloro-1-t-butylcyclohexane. At 80–97°, a 20% yield of 1-chloro-3-t-butylcyclohexane of at least 95% purity is obtained.

3. On the other hand, quite pure 1-chloro-1-t-butylcyclohexane (23% yield) is produced when boron fluoride is used at $0°$.

4. t-Butylcyclohexene (usually chiefly 1-t-butyl-1-cyclohexene) and chlorocyclohexane are by-products of the reaction in the presence of boron fluoride or bismuth chloride. The former is presumably produced by dehydrochlorination of the chlorobutylcyclohexane, the hydrogen chloride adding to cyclohexene to yield the chlorocyclohexane.

5. The proofs of structure of the two chlorobutylcyclohexanes are discussed. Incidental to their identification, two new ketones, 2- and 4-t-butylcyclohexanone, were synthesized and characterized by means of the semicarbazone derivatives.

Cross-linkage of Linear Polyesters by Free Radicals

BY W. O. BAKER

Introduction

The chemistry of rubber vulcanization and thermosetting of plastics has been hard to specify because relatively few bonds per unit volume are involved. This is notable in the statistics of chemical gelation.[1,2] The sensitivity of gelation reactions has apparently diverted attention to the fascinating array of organic by-products. This, in turn, has led to explanations of vulcanization as polar, colloidal, interfacial, etc., changes in the polymer, of great mystery and complexity. Such unclear interpretations persist, to some degree, despite excellent demonstrations of the physical effects of a few chemical cross-links.[3] Thus, in a review[4] of the multitude of different theories, it was said: "In the light of our present knowledge, it is probable that every type of vulcanization differs from every other type in the kind and extent of the various changes which together produce the vulcanized state." It is easy to see how the by-products, say, of olefin–sulfur reactions, and the general reactivity of double bonds, could inspire this statement.

Hence, it seemed worth-while to report briefly some observations made several years ago, on thermosetting and vulcanization of pure, linear polymers which contained no olefinic bonds nor complex functional groups. These were linear polyesters, and the reaction studied was with materials (chiefly benzoyl peroxide) which generate free radicals. The reaction mechanism therefore resembled those now so widely recognized in organic chemistry,[5] including that of "curing" agents. Such reactions were later applied to the vulcanization, in the sense of rubber technology, of polyester rubbers ("Paracon").[6,7,8] Likewise they were seemingly used with saturated acrylic esters (Lactoprene).[9]

With these polyesters, the thermosetting of plastics and the vulcanization of typical rubbers can be produced in virtually the same chemical composition. That is, by periodic insertion of methyl (or similar) groups the plastic is converted into a rubber.[7,10] Hence, with negligible change of chemical behavior the two curing processes may be identified with what is almost certainly a mechanism general for high polymers.

Since the details of the decomposition even of benzoyl peroxide itself are still under active study,[11] its effect on the saturated polymers will

(1) Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942).

(2) Stockmayer in "High Polymers," Reinhold Publishing Co., New York, N. Y., 1944.

(3) Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).

(4) Williams, "Chemistry and Technology of Rubber," A. C. S. Monograph No. 74, Reinhold Publishing Co., New York, N. Y., 1937, chap. VI. p. 237.

(5) Waters, *J. Chem. Soc.*, 409 (1946).

(6) Fuller and Biggs, meeting of Division of Rubber Chemistry, American Chemical Society, N. Y., Oct. 5, 1943, to be published.

(7) Biggs and Fuller, *Chem. Eng. News*, **21**, 962 (1943).

(8) Sumner and Myers, Meeting of Division of Rubber Chemistry, New York N. Y., Oct. 5, 1943.

(9) Mast, Rehberg, Dietz and Fisher, *Ind. Eng. Chem.*, **36**, 1022 (1944).

(10) Baker, *Rubber Chem. Tech.*, **18**, 632 (1945).

(11) For example, its decomposition depends on the chemical nature of its environment, as found in various solvents: Wieland, Ploetz and Indest, *Ann.*, **532**, 166 (1937); Wieland and Meyer, *ibid.*, **551**, 249 (1942); McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942). Recent important studies include Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946), and Cass, *ibid.*, **68**, 1976 (1946).

be shown mostly physically. The salient point is that the present results denote a special effect of the activity of many classes of high polymers, saturated as well as unsaturated, toward free radicals. Such processes may occur during aging and exposure as well as during compounding, casting and curing.

Experimental

Materials.—The linear polyesters were supercondensation polymers of definite, known structure.[12] All were prepared from chemically pure ingredients, in hydrogen atmosphere, as previously described.[13]

Where comparatively volatile components reacted, such as succinic acid and ethylene glycol, the reflux was carefully controlled during both esterification and ester-interchange, so that high molecular weights were obtained.

The polyundecanoates, chiefly studied, were readily freed from unsaturation by careful recrystallization of the ω-hydroxyundecanoic acid from dilute solution. Also, special care was taken to obtain succinic acid which did not decolorize potassium permanganate solutions on standing for up to an hour at room temperature. Absorption spectra in chloroform solutions had shown that even minute traces of, for instance, maleic acid, were easily detected by fading when aqueous solutions of the samples were added to dilute permanganate. Other dibasic acids were similarly tested, after purification by distillation, although their polymers will not be discussed much below. (This is because the behavior of, for example, polyethylene sebacate, polyethylene adipate, polydecamethylene sebacate, polyhexamethylene sebacate, and others was wholly analogous to that of polyethylene succinate, representing a high concentration of polar groups, on the one hand, and of polyundecanoate, with a dilute polarity, on the other.)

Benzoyl peroxide was recrystallized slowly from dilute benzene solution, so that large, perfect crystals free from any but (improbable) isomorphous impurities were produced, after washing. Solvents for the polymers were of reagent grade.

The reactions of the polymers with benzoyl peroxide were in small glass tubes, blanketed with heated carbon dioxide, and vigorously stirred by hand "pumping" of glass rods sliding through stoppers in the top. The polyester samples were put in these tubes and first melted in an electric furnace at 90°. The benzoyl peroxide was then added to the fluid mass as a saturated solution in benzene, and was quickly mixed into the mass as the benzene boiled off. This procedure seemed to avoid extensive premature decomposition of the peroxide. However, a definite decomposition was going on all the time. Also, presumably no foreign chemical elements were introduced, both carbon dioxide and benzene also being formed by the decomposition of benzoyl peroxide itself.

As the mass (weighing 1 g. or less) was thoroughly mixed, it was transferred to a furnace at 150° (for the experiments noted in Table I; other runs were done at 200° with similar, vastly quicker, results) for five minutes, and stirred constantly. The system was then quenched to room temperature. (With some polymers other than polyesters, heating briefly at 200–240° effected cross-linkage with less polymer degradation than longer heating with the peroxide, at lower temperatures.)

Measurements.—Viscosities of dilute chloroform solutions ($C = 0.4000$ g. polymer per 100 cc. soln.) were determined with precautions earlier noted.[13] Melt viscosities were obtained by the falling ball technique,[13] which was found to be the most convenient and accurate method over the range concerned.

Precipitabilities were checked both visually and photoelectrically as the point of non-solvent addition when there was the first *abrupt* change in turbidity[13] (*i. e.*, first actual phase separation). The initial concentration was always

1 g. of polymer per 100 cc. of chloroform and the volume fraction of non-solvent added to this solution at the turbid point is γ_0.

Simple creep tests were made on strips of rubbery polymers on which constant loads were hung. Observations were with a cathetometer, in a room at constant temperature (25°) and humidity (42% R. H.).

Results and Discussion

The simple chemical structure

$$HO \left[(CH_2)_{10}\overset{O}{\underset{\|}{C}}-O-(CH_2)_{10}\overset{O}{\underset{\|}{C}} \right]_n OH$$

·represents polyundecanoates. No functionality greater than 2 appears, in the ordinary sense.[14] However, the

$$-CH_2-\overset{O}{\underset{\|}{C}}-O-$$

group occurs frequently along the chains. The α-methylene hydrogens have been long recognized, in classical organic chemistry, as "active."[15] It was found that finely powdered benzoyl peroxide mixed with molten ($>83°$) polyundecanoates, and heated briefly at 100, 150 or 200° for five minutes), converted the fluid melts to thermoset, insoluble, gels. On cooling, these resumed the microcrystalline character of the original linear polyesters.[16] On heating again, this local order[17] was destroyed, *i. e.*, there was local "melting." However, no gross liquefaction or fluidity could be caused, even at high temperatures.

Apparently, a network of primary valence bonds had been produced by the benzoyl peroxide decomposition, roughly similar to its well known effect in the curing of *unsaturated* (maleic ester) casting resins, and the like. This cross-bonding was seemingly rare enough to allow crystallization of chain segments (doubtless a little less extensively than with the pure linear polymer), in the polyester below its "normal" melting point. The network greatly retarded, however, the *rate* of local ordering.[18] Nevertheless, an interesting state of matter was produced, which is locally crystalline, shows definite melting[18] on heating, but does not melt to a *liquid*. (This is also true of frozen, vulcanized rubber.)

Primary cross-bonds being formed in this comparatively simple system were thought to be between α-methylene groups in adjacent chains. For instance, the following reactions seem possible:[19-23]

(12) Carothers and Van Natta, This Journal, **55**, 4714 (1933).

(13) Baker, Fuller and Heiss, *ibid.*, 2142 (1941).

(14) Carothers, *Trans. Faraday Soc.*, **32**, 39 (1936).

(15) One of several recent investigations of the bond properties in such systems is by Gorin, Walter and Eyring, This Journal, **61** 1876 (1939).

(16) Fuller and Baker, *J. Chem. Ed.*, **20**, 3 (1943).

(17) Baker in "High Polymers," Reinhold Publishing Co., New York, N. Y., 1944.

(18) Thus, in such cross-bonded systems, the supercooling described for the linear materials was greatly enhanced; see Baker and Fuller, *Ind. Eng. Chem.*, **38**, 272 (1946). Such networks may also be a minor factor in the slow crystallization of polyester *rubbers*, on stretching, noted in ref. (10). Likewise, vulcanization is known to retard crystallization of rubber; Bekkedahl and Wood, *Ind. Eng. Chem.*, **33**, 381 (1941).
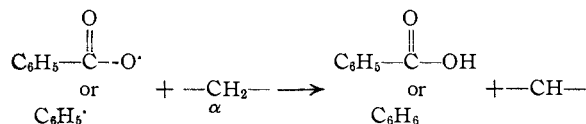
(19) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937), references therein.

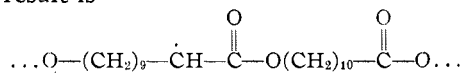(20) Gelissen and Hermans, *Ber.*, **59B**, 662 (1926).

(21) Reynhart, *Rec. trav. chim.*, **46**, 54 (1927).

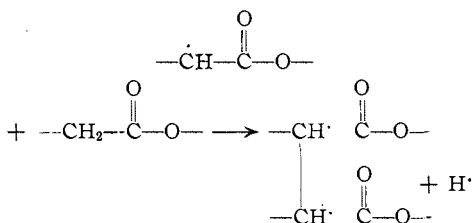(22) Farmer and Michael, *J. Chem. Soc.*, 513 (1942).

(23) Farmer, *Trans. Faraday Soc.*, **38**, 340 (1942).

$$C_6H_5-\overset{\overset{O}{\|}}{C}--O\cdot$$
$$\text{or} \quad + --CH_2-- \longrightarrow$$
$$C_6H_5\cdot \quad \quad \quad \alpha$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-OH$$
$$\text{or} \quad \quad +--CH--$$
$$C_6H_6$$

The result is

$$...O-(CH_2)_9-\overset{\cdot}{C}H-\overset{\overset{O}{\|}}{C}-O(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-O...$$

This "radical chain segment" above may then attack an adjacent polymer chain, as

$$-\overset{\cdot}{C}H-\overset{\overset{O}{\|}}{C}-O-$$

$$+ --CH_2-\overset{\overset{O}{\|}}{C}-O-- \longrightarrow --CH\cdot \quad \overset{\overset{O}{\|}}{C}-O--$$

$$-\overset{|}{C}H\cdot \quad \overset{\overset{O}{\|}}{C}-O-- \quad + H\cdot$$

This scheme is like (although not strictly analogous to) the chain transfer of wide application in olefin polymerizations.[24] Similarly (and more probably) two activated —CH— groups, in adjacent chains, might link together. Likewise, considerable benzoate substitution on the methylene groups is probable.[19,23]

Cross-Bonded Units.—However, it seems unlikely that many of the cross-links are —CH—
O—CH—, or other non-carbon–carbon bonds. An advantage of polyesters in studying vulcanization is that gentle but complete hydrolysis regenerates the original monomers. This has been done with various cross-linked, saturated polymers, and a small, but detectable, residue of material with functionality higher than 2, is found. Thus, a polyethylene succinate which was gelled with 4% of benzoyl peroxide at 150° was completely hydrolyzed by boiling with 0.5823 N hydrochloric acid. About 2.85% of the products (chlorine-free) resembled tetracarboxylic acids noted in the literature. Since the original peroxide concentration was 2.7% *molar* on the basis of ethylene succinate residues, and the radical linkage is presumably a chain reaction, this is a roughly reasonable yield of cross-bonds. They doubtless occur in fragments like

$$HOOC\cdot CH\cdot CH_2\cdot COOH$$
$$\overset{|}{HOOC\cdot CH\cdot CH_2\cdot COOH}$$
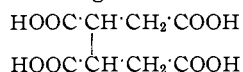
Formation of these bonds by means of free radicals resembles reactions of acetyl peroxide with glacial acetic acid,[25] and many similar examples currently being reported.

Limited Cross-bonding; Branching.—If the ideas so far noted are right, saturated polyesters should react with smaller quantities of benzoyl peroxide to give larger, branched, molecules, as the precursors of gelation. Accordingly, three

(24) Flory, THIS JOURNAL, **59**, 241 (1937).
(25) Kharasch and Gladstone, *ibid*, **65**, 15 (1943).

linear polyundecanoates, of increasing number-average molecular weight, M_n, were treated with various small quantities of benzoyl peroxide.

Typical results showing an apparent increase in average molecular size appear in Table I. (It should also be noted that there is *chain scission* as well as cross-linkage from these radical reactions. Its effect is thus averaged in Table I. In other experiments, it was possible to make breakdown exceed buildup, by operating at 250°, or with excesses of peroxide.)

Crucial for interpretation of these experiments was evidence that further esterification did not cause the changes found. Actually, numerous blank (without peroxide) runs with the temperatures and times noted always produced either no detectable change in the polyester, or slight *decrease* in viscosity. Likewise, benzoic acid (such as formed from the peroxide) added to the pure, molten polyester caused breakdown under the conditions used for peroxide reaction, rather than catalyzing condensation.

TABLE I

REACTION OF LINEAR POLYUNDECANOATES WITH BENZOYL PEROXIDE, AT 150°

Polymer	M_W	Wt. per cent. benzoyl peroxide added	$\dfrac{\ln \eta_r}{c}$	Precipitability, γ_0
U-A	8,000	0.0	0.314	0.574
U-A-1	....	2.61	.461	.534 (.535)
U-B	12,000	0.0	.434	.540
U-B-1	....	1.70	.634	.519
U-C	19,000	0.0	.675	.508
U-C-1	....	0.50	.873	.497 (.496)

All of the samples were examined carefully for actual gelation, and were quantitatively soluble except for about 1% of weak (highly swollen and therefore weakly netted) gel from sample U-C-1. This probably came from imperfect mixing of the peroxide, resulting in some locally high concentration.

The precipitabilities, γ_0, of these polymers are plotted in Fig. 1 against their inherent viscosities, before and after reaction. A couple of repeat determinations in Table I show the consistency of γ_0 values. A few points for linear polymers of different molecular weights are added to help define the curve. It is significant that the degrees of branching introduced by the free radical reactions do not change the relation between solubility (thermodynamic property) and dilute solution viscosity (kinetic property). This should be realized in considering the "anomalous" solution viscosity results so frequently attributed to branching by Staudinger and others. Indeed, since the materials U-A-1, U-B-1, etc., are theoretically near gelation,[2] it must be emphasized that some independent absolute measure of weight average molecular weight must be available in order to interpret dilute solution viscosity, at a
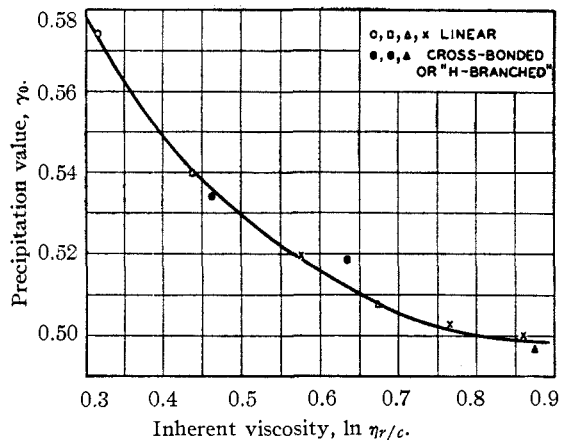
Fig. 1.—Relation between precipitation value γ_0 and inherent viscosity for polyundecanoates of varying structures.

given or limited concentration, and solubility as affected by branching.[26] (The *concentration dependence* of inherent viscosity is a different matter.[13,26]) Abnormal relations blamed on branching[27,28,29] may actually reflect changes in molecular weight distribution, or real network formation.

As expected, smaller amounts of peroxide are required for roughly similar increments in inherent viscosity, the greater the original chain length.

Branching and Melt Viscosity.—Similarly, polyesters branched by use of tri-functional glycols and acids behaved like linear molecules when their dilute solution viscosities were plotted against melt viscosities.[30] However, it should be emphasized that, by contrast, branching of chains, at least at higher polymerization levels than those reported,[30] *does* ultimately affect melt viscosity. For instance, in Fig. 2 are plotted the melt viscosities, at 90°, of polyethylene sebacates, against their intrinsic viscosities $[\eta]$. The lower curve is for strictly linear molecules (and would give, of course, a linear plot of log η vs. $[\eta]^{1/2}$).[13] The upper curve is for degrees of condensation leading to values of $[\eta]$ overlapping those on the lower. However, in ascending order, 0.5, 1.0 and 1.5 mole per cents. of glycerol replaced part of the ethylene glycol. Notably higher values of melt viscosity, for given $[\eta]$ values, were likewise found for polyesters reacted with free radicals, short of gelation. Thus, dilute solution viscosity ap-

(26) On the other hand, dispersed particles which are actually *netted* or gelled (microgel) show characteristic decline in ln$\eta r/c$; and change in d (ln$\eta r/c$)/dc; see Baker, "Structure of Synthetic Rubber, A. A. A. S. Conferences on Chemistry, Gibson Island, Md., July 4, 1946," to be published.

(27) Staudinger and Schneiders, *Ann.*, **541**, 151 (1939).

(28) Staudinger and Schmidt, *J. prakt. Chem.*, **155**, 129 (1940).

(29) Staudinger and Nuss, *ibid.*, **157**, 283 (1941).

(30) Weil, Stockmayer and Beckmann, "Melt and Solution Viscosities of Branched Polyesters," Division of Physical and Inorganic Chemistry, American Chemical Society, Atlantic City, N. J., April 11, 1946.

parently rises proportionately much less than melt viscosity, as gelation is approached. Melt viscosities, or those of concentrated solutions, compared to dilute solution properties, may be convenient empirical probes to study branching caused by free radical reactions.
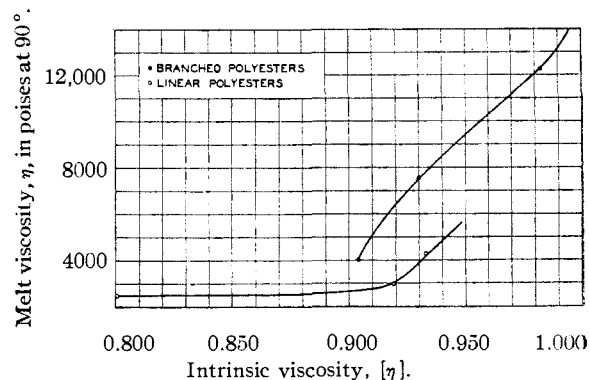

Fig. 2.—Effect of branching on relation between melt viscosity and dilute solution viscosity of polyethylene sebacates.

The effect of benzoyl peroxide reacted still further with polyethylene sebacate, to gelation, is illustrated in Fig. 3. Here, a lower temperature, 135°, and a larger concentration of peroxide (5 per cent. by wt.) permitted slower observations. Some small gas bubbles were formed during peroxide decomposition. Beginning with a fairly low η, the system thickened steadily, until high elasticity obscured viscous flow, and the measurements were discontinued. The jump from the still comparatively low η of 4500 poises to the
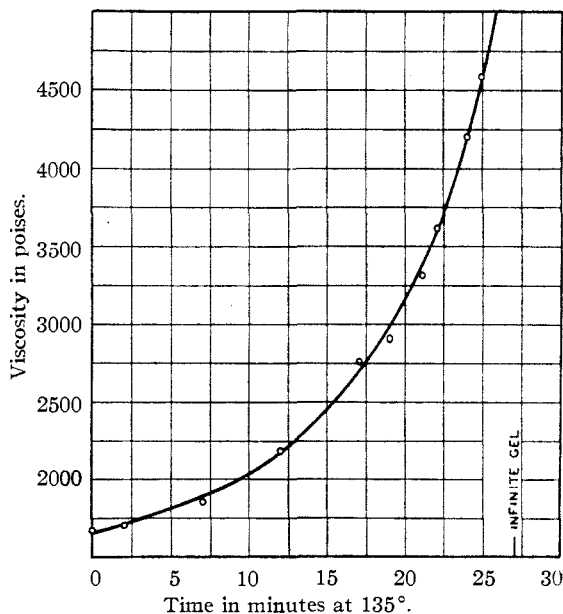

Fig. 3.—Reaction of polyethylene sebacate with benzoyl peroxide shown by increase in melt viscosity before gelation.

gel point agrees with the general principles of gelation theory.[1,2] Again, the peroxide seems to have caused numerous cross-links in the saturated polymer. Correspondingly, the product had become mostly insoluble in all solvents. Similar results were found with lauryl and stearyl peroxides, tertiary butyl hydroperoxide and other sources of free radicals.

Cross-linkage of Saturated Polyester Rubber.—The other test to show primary valence cross-bonds from reaction with benzoyl peroxide was on a rubbery system.[7,10] Here, the effect of cure on high elasticity—the crux of rubber vulcanization—could be followed. Polypropylene sebacate copolymer containing 20 mole per cent. ethylene glycol units and of $M_w \sim 20,000$ is a boardy gum which, when uncrystallized, creeps steadily under constant load. At room temperature it retains stress for only a few seconds. If cross-linked into an essentially infinite network, and in the absence of chemical reactions which split the chain segments, it should not creep appreciably after elongation under constant load. A strip of such rubber, filled with 75 parts by weight of calcium carbonate, reacted with 5% (of the polymer weight) of benzoyl peroxide, in a conventional rubber test sheet mold. It was then observed, at 25°, under constant loads causing in one case 48% and, in another, 104% elongation. The change in this elongation with time appears in Fig. 4, and is remarkably slight, indicating extensive primary valence networks, in contrast to the uncured gum.

On Fig. 4, the tensile creep with constant load is plotted as S/S_0, from the kinetic theory of rubbery elasticity.[31] That is

$$S/S_0 = \frac{\dfrac{l_0}{l_u} - \left(\dfrac{l_u}{l_0}\right)^2}{\dfrac{l}{l_u} - \left(\dfrac{l_u}{l}\right)^2}$$

where

S_0 = number of network chains initially (time $t = 0$)
S = number of network chains at time t
l_0 = sample length at time $t = 0$
l = sample length at time t
l_u = sample length before stretching

Since the data for Fig. 4, at 25°, are in a temperature range where secondary bonds are virtually all unstable (as shown by viscous flow of uncured sample), the comparatively small slope of the curve indicates that a primary valence network has indeed been formed by the peroxide reaction. Alternate interpretations of creep lead to similar results.[32]

Likewise, the percentage "permanent set" in samples elongated 104% for as much as three hundred and thirty-nine hours was only 5% immediately after unloading, 3% one hour later, and declined to about 2% standing, still at room temperature, overnight.

(31) Tobolsky and Andrews, J. Chem. Phys., **13**, 3 (1945),
(32) Mooney, Wolstenholme and Villars, J. Applied Phys., **15**, 324 (1944); see also comments of Stevens, India-Rubber J., **108**, 517 (1945).
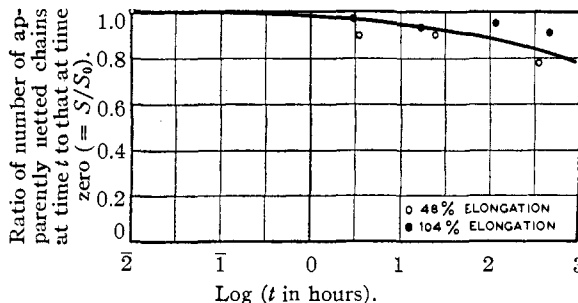
Fig. 4.—The small continuous creep, under constant load, of polypropylene–ethylene sebacate after cross-linkage with benzoyl peroxide.

Implications.—Since many linkages (including polar and olefinic) activate α hydrogen atoms in organic molecules, free radicals may be expected to react this way with many saturated as well as unsaturated chain polymers. The detailed structure of the polymer will decide whether simple substitution, chain scission or cross-linkage finally results. Many vulcanization processes probably have free radical mechanisms,[33] and hence do not have to depend on activation of residual double bonds. Even when copolymers contain a few residual double bonds per chain, these may react with *saturated* groups in adjacent chains. Thus, double bonds would not have to be lined up, in an improbable way. Likewise, aging of plastics and rubbers, while often predominantly a chain degradation, may include oxidation mechanisms[34,35] leading to cross-linkage. This has been found, for instance, in the high temperature aging of cellulose esters.

Indeed, in a general lecture on polymers it was said "...nearly all long chain molecules can be cross-linked."[36] It is hoped that the present specific results on a simple, saturated system will add to the significance of this remark.

Acknowledgment.—I wish to thank Dr. C. S. Fuller for drawing attention to the problem of "curing" reactions.

Summary

Compounds decomposing to give free radicals, such as benzoyl peroxide, react with saturated linear polyesters such as polyundecanoates. Cross-linked, thermoset systems, which often still retain microcrystallinity, are ultimately formed. Probably methylene groups α to the ester group are activated by losing a hydrogen atom to a free radical. Two such —CH— groups may then combine to form a cross-bond, or they may attack other α-methylene groups.

Polyundecanoates reacted with small quantities of benzoyl peroxide, short of gelation, yield species

(33) See review by Alfrey, Hendricks, Hershey and Mark, India Rubber World, **112**, August and Sept. (1945).
(34) Farmer, Bloomfield, Sundralingam and Sutton, Trans. Faraday Soc., **38**, 348 (1942).
(35) Farmer, Trans. Inst. Rubber Ind., **21**, 122 (1945).
(36) Naunton, India-Rubber J., **108**, 492 (1943).

whose precipitabilities plotted against their dilute solution viscosities lie on the same curves which are characteristic of the original *linear* polyesters. Hence, the relation between dilute solution viscosity and solubility is not sensitively affected by branching. (However, the relations of these properties to molecular weight are apparently changed.)

Further, actual thermosetting of polyester plastics and vulcanization of polyester rubbers is shown, by viscosity and creep experiments, to follow from these simple free-radical reactions. Similar processes are suggested for aging, "oxidation" and other reactions of chain polymers containing little or no olefinic unsaturation.

MURRAY HILL, N. J.   RECEIVED NOVEMBER 27, 1946

A Spectrophotometric Study of the Hafnium–Alizarin Lake

BY HERMAN A. LIEBHAFSKY AND EARL H. WINSLOW

The constitution of hydroxyanthraquinone lakes has always been a lively topic—in the beginning, because of the relation of these lakes to mordant dyeing, and more recently in connection with their formulation as chelate compounds. As a sequel to earlier work,[1] we have studied spectrophotometrically the formation of the hafnium–alizarin lake, which is so stable in acid solution that it serves well for the estimation of hafnium. Needless to say, the problem is exceedingly complex, not only owing to the nature of the reactants but also because the lakes as finally measured are colloidal suspensions. These complications should tend to disappear with increasing dilution, and there is consequently some hope of obtaining results simple enough to be interpreted from work on a microgram scale; but one can scarcely expect definitive answers to all the questions involved. The experimental method has already been described.[1]

Lake formation was investigated under three sets of conditions: (1) with hafnium in excess (Fig. 1), (2) with hafnium and alizarin comparable (Fig. 2), (3) with alizarin in excess (Figs. 3 and 4), the last being the standard condition for the spectrophotometric estimation of hafnium. The principal evidence on the constitution of the lake in question will be obtained by using derived data from Figs. 1 and 3 to interpret Fig. 2, in which the
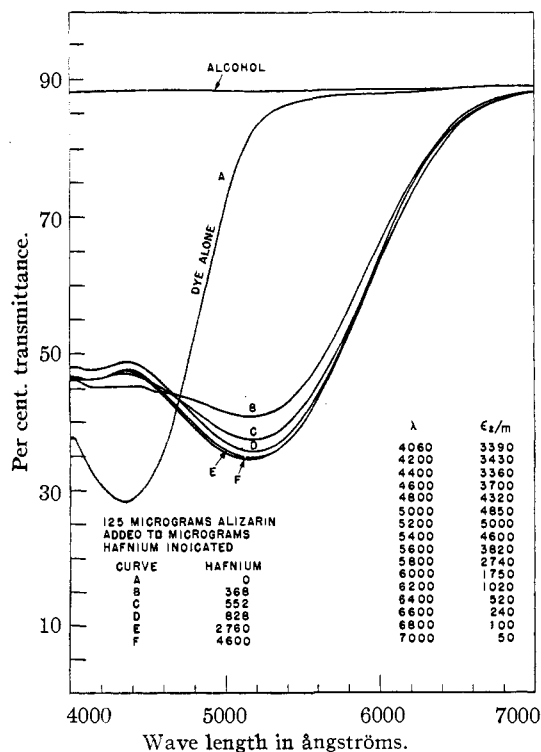

Fig. 1.—Transmission curves for lake formation with hafnium in excess.
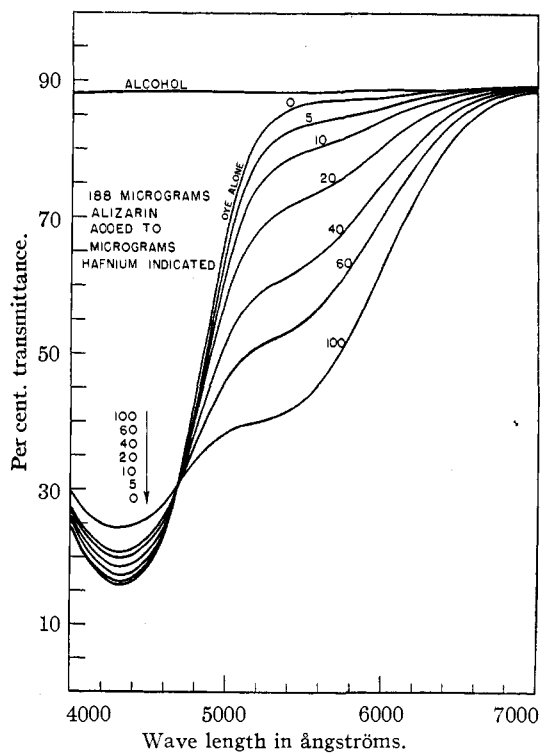
(1) Liebhafsky and Winslow, THIS JOURNAL, **60**, 1776 (1938).

Fig. 2.—Transmission curves for lake formation with hafnium and alizarin comparable.