demonstrated that a variety of breakdown products (such as formaldehyde and carbon dioxide) are produced during this type of cellulose oxidation, indicating that the oxidizing agent is not confined in its action to oxidation at the number two and three carbon atoms of the anhydro-glucose unit, this hypothesis may be viewed with some reserve. Head[19] recently has shown that in both mono- and polysaccharides, dialdehydes are converted to carboxyl slowly in the presence of dilute alkali.

The criticisms of Davidson and Purves on the calcium acetate method for carboxyl determination do not appear valid when the method is used for celluronic acids.

While this paper was being prepared, an investigation appeared of the structure of celluronic acids by absorption spectra.[20] The data indicate large contents of carboxyl groups with possibly a small carbonyl group content. These results agree with our chemical findings.

Summary

1. Potentiometric investigations show that celluronic acids degrade in alkaline solutions to generate acidity.

2. Small amounts of carbonyl groups appear to be present in the celluronic acids.

3. The acidity generated in alkaline solution at a constant reaction time appears directly related to the carbonyl group content and is an exponential function of the alkali concentration.

4. The ketone groups are believed to enolize in alkali, the enediols split as in simple carbohydrates, the adjacent glucoside links hydrolyze and an extensive alkaline degradation is thus initiated which continues along the chain producing reducing and acidic substances.

ROCHESTER 4, NEW YORK RECEIVED FEBRUARY 24, 1948

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[19] Head, *Shirley Inst. Mem.*, **21**, 11 (1947).

[20] Rowen, Hunt and Plyler, *J. Research Natl. Bur. Standards*, **39**, 133–140 (1947).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Migration of Acetyl and Benzoyl Groups in *o*-Aminophenol

BY ARTHUR L. LEROSEN AND EDGAR D. SMITH

A considerable amount of experimental data has been collected on the general subject of acyl migrations in *o*-aminophenols since interest was first drawn to this problem by Stieglitz[1] in 1898. The great majority of this work has been published by Raiford and co-workers[2–4] and has indicated that when two different acyl groups, derived from carboxylic acids, are introduced into an *o*-aminophenol generally the same acyl derivative is obtained regardless of the order of introduction. On hydrolysis the heavier acyl group has usually been found on nitrogen.

No satisfactory general explanation has been given for all the phenomena observed in the acylation or hydrolysis of these compounds. The best discussion to date, in the opinion of the authors, was that of Bell,[5] and this work has generally been neglected by other workers in this field.

The present work was undertaken because it seemed probable that it would be possible to give an adequate explanation of these acyl migrations in terms of a combination of the theory of resonance and inductive effects. Accordingly a general theory was derived for these reactions and was found to agree in many respects with the data found in the literature. Nevertheless there were discrepancies and these were of such a nature that a reëxamination of the reported data was advisable, especially since at present new and powerful aids to this study are available in the form of absorbtion spectroscopy for the determination of structure, and chromatographic techniques for the quantitative analysis of mixtures.

It is premature to present the details of our theories of acyl migrations here, but three resulting conclusions are important: first, no migration should be complete, but instead there should be a reversible equilibrium; second, in the acetyl–benzoyl migration the N-acetyl isomer should predominate; and third, if a "migration" occurs in acylation, the opposite migration should be observed during hydrolysis. There are no conclusive data on this first point in the literature, Raiford found only one product in the acetyl–benzoyl mixed acyl derivative, while Bell reported the formation of different isomers, depending on the acylation sequence. Bell based his conclusions on mixed melting point data. Both of these men reported that hydrolysis yielded only *o*-benzoylaminophenol.

The experiments here were concerned with the determination of the nature of the acylation product when acetyl and benzoyl groups were introduced into *o*-aminophenol in different sequence. The method was to prepare the crude derivatives by acylation with the corresponding anhydrides in pyridine solution, and to separate the product into its constituents chromatographically. The determination of structure was accomplished by comparison with spectroscopic curves determined for all of the possible mono- and diacyl deriva-

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[1] Julius Stieglitz, *Am. Chem. J.*, **21**, 111 (1898).

[2] L. C. Raiford, THIS JOURNAL, **41**, 2068 (1919).

[3] L. C. Raiford and J. R. Couture, *ibid.*, **46**, 2305 (1924); **44**, 1792 (1922).

[4] L. C. Raiford and H. P. Lankelma, *ibid.*, **47**, 1111 (1925).

[5] Frank Bell, *J. Chem. Soc.*, 2966 (1931).

tives of *p*-aminophenol using acetyl and benzoyl groups.

Our experimental results show that two mixed diacyl derivatives are present in both crude products which, however, are predominantly N-acetyl-O-benzoyl and N-benzoyl-O-acetyl depending on the acylation sequence. Acetylation of *o*-benzoylaminophenol gave 91% of the unrearranged N-acetyl-O-benzoyl derivative, while benzoylation of *o*-acetylaminophenol gave 62% of the unrearranged isomer. Both of the pure mixed diacyl derivatives were isolated in their pure form for the first time and their physical properties and relative stabilities under the influence of several factors were studied.

Solution of either of the isomeric mixed diacyls in alcohol or pyridine produced equilibrium mixtures containing 85 and 77% of the more stable N-acetyl-O-benzoyl form, respectively. Water and heat also served to isomerize these diacyls, while benzene, hexane, acetone, ethyl ether and dioxane were much less effective, if not inert, in this respect. It seems probable that this is a case of general acid and base catalysis.[6]

The absorption curves of the derivatives studied are shown in Fig. 1. It will be noted that the total area under the curves roughly indicates the number of phenyl groups in the molecule, while whenever a N-benzoyl structure is present, one of the peaks (previously superimposed) shifts to longer wave lengths. No attempt will be made here to interpret these curves in terms of theory, but it may be indicated that they offer a good possibility of interpreting the peaks in terms of the contributions of the different resonating structures. The spectra for the mixed diacyls were determined in hexane to avoid the isomerization which occurred in alcohol and these curves are shown in the figure. The absorption spectra of the other acyl derivatives of *o*-aminophenol are not shown since there was no essential change from the spectra found in alcohol. The wave lengths and molar extinction coefficient in both of these solvents is, however, included in the tabulation shown in Table V.

The analytical data are summarized in Tables I through IV below. Table I shows the analyses obtained on the crude products of the acylations in pyridine solution, and also the analysis of these two products after a single recrystallization from alcohol.

Table I

Analysis of Ortho Mixed Diacyls

Sample description	Reaction yield, %	Product analysis[a] %NA[b]	%NB[c]	% Recovery
Crude NB	98	38	62	91
Crude NB	98	37	63	94
Crude NA	84	91	9	94
Crude NA from 50% alc.	..	93	7	94
Crude NB from 50% alc.	..	82	18	95

[a] Analyses based on amount of sample recovered by elution of the bands with acetone. [b] N-acetyl-O-benzoyl-*o*-aminophenol. [c] N-benzoyl-O-acetyl-*o*-aminophenol.

Table II shows the analyses found on the residual products obtained by dissolving mixed diacyl samples of varying composition in a few ml. of alcohol and then evaporating off the solvent under vacuum. It will be seen from this table that the isomerizations in alcohol were complete for all except the pure N-benzoyl-O-acetyl isomer. No explanation can be given here for the peculiar behavior of this isomer, but it may be significant that the sample recovery in these runs was consistently low.

Table II

Analysis of Alcohol Isomerization Products

Sample description	Standing time, hr.	Product analysis[a] %NA[b]	%NB[c]	% Recovery
Pure NA	0	85	15	107
91% NA	0	83	17	87
38% NA	0	84	16	89
38% NA	0	85	15	93
Pure NB	0	57	43	...
Pure NB	2	71	29	87
Pure NB	3.5	72	28	85

[a] Analyses based on amount of sample recovered by elution of the bands with acetone. [b] N-acetyl-O-benzoyl-*o*-aminophenol. [c] N-benzoyl-O-acetyl-*o*-aminophenol.

Table III shows the results of similarly dissolving the mixed diacyls in pyridine and then evaporating off the solvent under vacuum after allowing the solutions to stand for the length of time indicated. It will be seen that the isomerizations were slightly less rapid than those obtained in alcohol, and that the equilibrium mixture formed had a slightly different composition.

Table III

Analysis of Pyridine Isomerization Products

Sample description	Standing time, hr.	Product analysis[a] %NA[b]	%NB[c]	% Recovery
Pure NA	6	77	23	98
Pure NA	0	86	14	106
91% NA	3	77	23	95
38% NA	3	75	25	94
Pure NB	6	77	23	98
Pure NB	0	81	29	94

[a] Analyses based on amount of sample eluted by acetone. [b] N-acetyl-O-benzoyl-*o*-aminophenol. [c] N-benzoyl-O-acetyl-*o*-aminophenol.

Table IV shows the results of heating the two pure isomers for varying lengths of time at two different temperatures near their melting point. While the results of these runs are inconclusive since equilibrium was not reached in either of these runs, it appears that, as expected, the N-acetyl-O-benzoyl compound isomerized much more slowly than its isomeride.

In conclusion, it seems that the predictions of theory have been verified for the first two of the possibilities mentioned above, and that the con-

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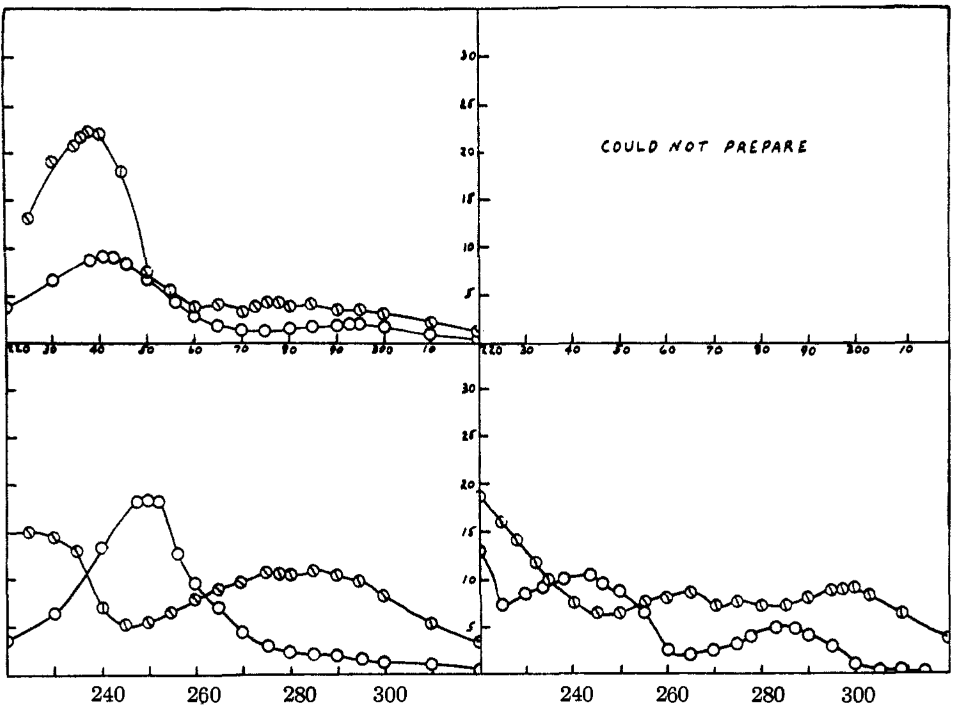
(6) L. P. Hammett, "Physical Organic Chemistry," 1st ed., McGraw-Hill Book Co., New York, N. Y., 1940, pp. 215-227.

Para series: O, O-acetyl in alcohol; ⊘, O-benzoyl in alcohol.

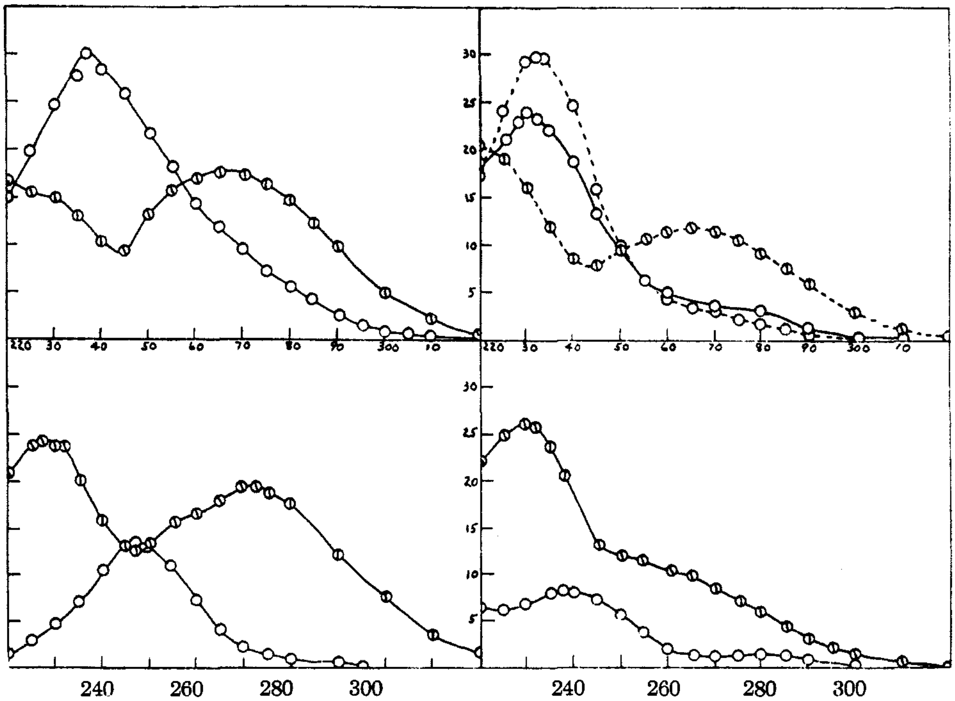
Ortho series: Could not prepare.



O, N-acetyl in alcohol; ⊘, N-benzoyl in alcohol.

O, N-Acetyl-O-benzoyl in alcohol; ⊘, N-benzoyl-O-acetyl in alcohol.

O—O, Alcohol equilibrium mixture: O—O, N-acetyl-O-benzoyl in hexane; ⊘---⊘, N-benzoyl-O-acetyl in hexane.



O, Diacetyl in alcohol; ⊘, dibenzoyl in alcohol.

Fig. 1.—Ultraviolet absorption spectra of acyl derivatives of *o*-aminophenol and *p*-aminophenol. The ordinate is the molecular extinction coefficient $(\epsilon) \times 10^{-3}$, and the abscissa is the wave length in millimicrons.

Table IV

Effect of Heat on Pure Mixed Diacyls

Sample description	Temp., °C.	Standing time, hr.	Product analysis[a] %NA[b]	%NB[c]
Pure NA	140	2	69	31
Pure NB	140	2	59	41
Pure NA	132	70	61	39
Pure NB	132	70	54	46

[a] Analyses based on amount of sample recovered by elution with acetone. [b] N-acetyl-O-benzoyl-*o*-aminophenol. [c] N-benzoyl-O-acetyl-*o*-aminophenol.

flicting results obtained by Raiford and Bell may be explained as being due to the use of alcohol as a recrystallization solvent by the former. In such a case isomerization would occur, leading to the isolation of the predominant isomer, in this instance the N-acetyl-O-benzoyl compound. It now seems desirable to reëxamine much of the past work in this field in the light of these facts. We are continuing this study at present.

Experimental

Preparation of Compounds.—The acyl derivatives studied are listed in Table V. Except as noted in the table, they were prepared by heating a pyridine solution of the aminophenol with a 10% excess of the acid anhydride for about thirty minutes on a steam-bath. The product was isolated by cooling the solution and pouring it into ice water. With the exception of the mixed *o*-acyl derivatives the products were purified by crystallization from alcohol.

Table V

Acyl Derivatives Studied

Compound	Melting point, °C. (cor.) Found	Literature	Ultraviolet abs. maxima λ	$\epsilon^{f} \times 10^{-3}$
p-Aminophenyl-benzoate[a]	153–155	153[7]	239	22.5
p-Aminophenyl-acetate[b]	70–72	75[8]	241	9.2
p-Acetylaminophenol	166	166[9]	250	18.5
p-Diacetylaminophenol	150	152[10]	247	13.5
p-Benzoylaminophenol	214–216	227,[7] 205[11]	225	15.0
		215,[12] 227[13]	285	11.0
p-Dibenzoylaminophenol	233–235	235[14]	228	24.2
			271	19.5
N-Benzoyl-O-acetyl-*p*-aminophenol	172–174	171[15]	220	18.0
			268	18.0
N-Acetyl-O-benzoyl-*p*-aminophenol	167–169	167,[13] 171[15]	237	30.0
o-Acetylaminophenol	203–204	201–204[16]	242	10.5
	207–208[c]		284	5.0
			235[d]	6.9
			283[d]	3.0
o-Diacetylaminophenol[e]	124–125	124–125[17]	238	8.0
			240[d]	12.0
o-Benzoylaminophenol	170–171	168[18]	265	8.4
			296	8.6
			222[d]	17.8
			295[d]	8.0
o-Dibenzoylaminophenol	183–185	182–185[19]	230	26.0
			229[d]	30.0
			266[d]	12.5
N-Benzoyl-O-acetyl-*o*-aminophenol	138–140	134–138[2]	230	23.9[g]
		125–127[5]	220[d]	20.3
			265[d]	12.5
N-acetyl-O-benzoyl-*o*-aminophenol	139–141	134–138[2]	230	23.9[g]
		132–135[5]	232[d]	30.0

[a] Prepared by reduction of corresponding nitro compound with $SnCl_2$. [b] Prepared by method of Galatis[8] except that tar formation and resultant necessity of vacuum distillation was eliminated by the addition of a few crystals of hydroquinone and sodium bisulfite before neutralizing the acid hydrolysis mixture with sodium bicarbonate. [c] This high melting compound was prepared during an attempted acetylation of benzylidine *o*-aminophenol. It gave the same spectra as, and raised the melting point of, the 204° compound. [d] Refers to the absorption maxima found in hexane. All other absorption data were taken in alcohol. [e] The usual acylation method gave a mixture of mono and diacetyl derivatives which proved very difficult to separate. This compound was therefore prepared by heating the usual mixture of reactants under reflux for one and one-half hours, and then evaporating pyridine solution until crystals separated. [f] Molar extinction coefficient. [g] Alcohol equilibrium mixture.

Isolation and Purification of Mixed *o*-Acyl Derivatives.—It was found impractical to purify the mixed diacyl derivatives of the ortho series by recrystallization procedures since, in alcohol, isomerizations occurred, while in the other solvents tried the solubilities of the two isomers were too similar. These crude products were therefore chromatographed from benzene solution on a column of 1:1 silicic acid and Cellite using a 1.5% solution of acetone in benzene as the developing agent. The adsorbate zones were located by streaking the column first with a 3% solution of *p*-methoxybenzenediazonium fluoroborate, and then with a 5% solution of potassium hydroxide in methanol. This combination produced a distinct orange color with both isomeric mixed diacyls which could be further intensified by a third streaking with 6 *M* hydrochloric acid which caused the orange color to change to a deep red. The streaked areas were cut away, the column divided into the two sections containing the acyl derivatives, and the pure isomers recovered by eluting them from the adsorbent with acetone. (Determination of the ultraviolet absorption spectra of the two materials in hexane showed that the top zone was the N-acetyl-O-benzoyl derivative.)

Analysis of Diacyl Mixtures.—The crude mixture of isomers was chromatographically separated as outlined above, but, before eluting, the two portions of the adsorbent containing the pure isomers were powdered and dried under vacuum to remove any solvent which might absorb in the ultraviolet. The isomers were then eluted with

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(7) H. Hübner, *Ann.*, **210**, 378 (1882).

(8) L. Galatis, *Ber.*, **59**, 850 (1926).

(9) A. Lumière, *et al.*, *Bull. soc. chim.*, [3] **33**, 785 (1905).

(10) Beilstein, "Handbuch der organischen Chemie," Vol. IV, xiii, 1930, p. 464.

(11) A. W. Smith, *Ber.*, **24**, 4042 (1891).

(12) F. Reverdin and E. Delétra, *ibid.*, **39**, 125 (1906).

(13) J. B. Tingle and L. F. Williams, *Am. Chem. J.*, **37**, 51 (1907).

14) Beilstein, ref. 10, p. 470.

(15) F. Reverdin. *Ber.*, **39**, 3793 (1906).

(16) Beilstein, ref. 10, p. 370.

(17) E. Bamberger, *Ber.*, **36**, 2050 (1904).

(18) Beilstein, ref. 10, p. 372.

(19) Beilstein, ref. 10, p. 373.

absolute alcohol and the resulting solutions quantitatively determined by comparing their ultraviolet absorption at 230 millimicrons with that found for 0.01 *M* solutions of the mixed acyls.

Determination of Ultraviolet Absorption Curves.—All ultraviolet absorption data shown in Table V were taken on a Beckmann Ultra Violet Spectrophotometer, Model DU. Hundredth molar solutions of each acyl derivative were made up, and these solutions diluted as became necessary by pipetting a 1-ml. aliquot and diluting to 10 ml. No attempt was made to calibrate the volumetric flasks or pipets used.

In hexane solution, due to the extreme insolubility of the acyl derivatives, it was necessary to determine the spectra of the saturated solutions of the compounds in this solvent. The concentrations of these solutions were found by pipetting a 10-ml. aliquot, evaporating to dryness under vacuum, and taking up the residue in 10 ml. of absolute alcohol. The concentration of this alcohol solution, and hence that of the hexane solution, was then determined by comparing its ultraviolet absorption intensity at 230 millimicrons with that of an alcohol solution of known concentration.

Summary

1. In the benzoylation of N-acetyl-*o*-aminophenol and the acetylation of N-benzoyl-*o*-aminophenol, mixtures of the two possible isomers were obtained showing that a partial rearrangement occurred in each case. These mixtures were quantitatively separated by chromatography, and the identity of the two isomers established by comparison of their ultraviolet absorption spectra with that of the corresponding derivative of *p*-aminophenol.

2. It has been shown that alcohol, pyridine, water and heat cause either pure mixed diacyl derivative to isomerize to yield an equilibrium mixture of the two isomers. In alcohol and in pyridine solutions an equilibrium mixture containing 85 and 77%, respectively, of the N-acetyl-O-benzoyl form was obtained. It was pointed out that this isomerization in alcohol probably accounts for the conflicting results reported by Raiford and by Bell.

3. In the light of the above facts it seems desirable to reëxamine much of the past work in this field.

BATON ROUGE, LOUISIANA RECEIVED MARCH 1, 1948

[CONTRIBUTION NO. 149 FROM THE GOODYEAR TIRE AND RUBBER CO. RESEARCH LABORATORY]

Synthesis of Multichain Polymers and Investigation of their Viscosities[1]

BY JOHN R. SCHAEFGEN AND PAUL J. FLORY

Polymerizations in which the structural units are combined in other than strictly linear sequences generally yield gelled, insoluble products owing to the eventual formation of infinite network structures. Established exceptions are so few that thermoplasticity and solubility have sometimes been regarded as exclusive characteristics of linear polymers. On the other hand, nonlinear structures have been postulated on various occasions for some of the thermoplastic vinyl polymers,[2,3] and it has been recognized,[4] in principle at least, that monomer units may be assembled in non-linear patterns which do not lead to network formation and the manifestations of gelation resulting therefrom. Chain transfer with previously formed polymer molecules in vinyl polymerizations doubtless leads to some degree of branching without producing network structures.[5-7] However, the extent of such branching, like the cross-linking produced in diene polymers, is not easily measured or controlled.

Effects of departure from linear structure on physical properties of non-gelled polymers have been the subject of frequent speculation, but little information of a quantitative nature is available as a result of the difficulty of isolating the nonlinearity variable. In the first place, the extent of branching or of cross-linking (prior to gelation) in the polymer as a whole usually is difficult to estimate quantitatively. Secondly, such reactions ordinarily occur in a random manner such that the co-existing polymer molecules vary widely in degree of non-linearity, ranging from linear to highly branched structures. Finally, random cross-linking and branching reactions usually broaden the molecular weight distribution, sometimes severely; consequently, alteration of the molecular weight distribution, rather than nonlinearity, may be primarily responsible for the effects observed.

In the present investigation a convenient general procedure for synthesizing non-linear condensation polymers of controlled structure has been demonstrated. The principle employed here involves the co-reaction of an A—B type monomer, *e.g.*, an amino acid or hydroxy acid, with a small proportion of a multifunctional reactant of the type RA_b or RB_b where R is a *b*-valent radical and A and B are co-reacting functional groups; such multifunctional reactants may be, for example, a polyamine or a polybasic acid. Polymers so produced can be represented by the formulas

$$R[-A(B-A)_{\bar{y}}-]_b \quad \text{or} \quad R[-B(A-B)_{\bar{y}}-]_b$$

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[1] Presented before the High Polymer Forum at the New York Meeting of the American Chemical Society, September, 1947.

[2] G. V. Schulz, *Z. physik. Chem.*, **B44**, 227 (1939); H. Staudinger and G. V. Schulz, *Ber.*, **68**, 2320 (1935); H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

[3] H. Mark and R. Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 191, 219, *et seq.*

[4] H. W. Melville, *Trans. Faraday Soc.*, **40**, 217 (1944).

[5] P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

[6] P. J. Flory, *ibid.*, **69**, 2893 (1947).

[7] R. B. Carlin and N. E. Shakespeare, *ibid.*, **68**, 876 (1946).