Retardation and chain transfer were studied in the polymerization of styrene by stannic chloride catalyst in carbon tetrachloride–nitrobenzene solvent mixture. The data were correlated by means of the aforementioned equation which may be written as

$$\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_{no}} = \frac{k_r}{k_p}\frac{[R]}{[M]} \qquad (2)$$

$[R]/[M]$ represents the mole ratio of retarder or chain transfer agent (R) to monomer, k_r/k_p the ratio of the rate constant for reaction of ion pair with R to the propagation rate constant, and the terms $\bar{P}_n$ and $\bar{P}_{no}$ the number average degree of polymerization in the presence and absence of R, respectively.

For each compound reported in Table I polymerizations were carried out at about six different concentrations of R, and at least two control polymerizations containing no R were carried out at the same time. The concentrations of monomer, catalyst and nitrobenzene were the same in all runs, and the total volume per cent. of carbon tetrachloride plus R was also maintained constant.[2]

Polymerizations were ordinarily stopped at 10–15% conversion by precipitation of the polymer in methanol. The degrees of polymerization were determined from measurements of intrinsic viscosities in benzene solution at 30°, using the intrinsic viscosity–molecular weight relation of Pepper[3] for unfractionated polystyrene. $\bar{P}_{no}$ is about 200 under the conditions of our experiments, and the concentrations of R were chosen over a range so that at the highest concentration $\bar{P}_n$ was about one-third to one-half of $\bar{P}_{no}$.

In each case a plot of $1/\bar{P}_n - 1/\bar{P}_{no}$ *vs.* $[R]/[M]$ is linear and passes through the origin. The values of k_r/k_p obtained from the slopes of these plots are listed in Table I, together with relative values of k_r. These values are consistent with the mechanism proposed (1), based on qualitative knowledge of the Friedel–Crafts reaction.

TABLE I

POLYMERIZATION DATA[a]

Compound (R)	k_r/k_p	k_r (relative) neucleophilicity factor[b]
p-Cymene	0.0044	0.42
p-*t*-Butyltoluene	0.0062	0.69
p-Chloroanisole	0.0082	0.78
p-Xylene	0.0105	1
Thiophene	0.98	93
Anisole	1.62	154

[a] Initial monomer concentration = 1.95 *M;* stannic chloride concentration = 0.023 *M;* temperature 0°. [b] The value of k_p is assumed to be identical in all cases; a value of k_r = 1 is arbitrarily assigned to *p*-xylene.

Relative rates of polymerization were measured in the absence and presence of additional compounds, using a precipitation technique. Over the measured range, about 10–80% conversion, under the conditions employed here the reaction is pseudo first order with respect to monomer.

The hydrocarbons have little or no effect on the rate, indicating that only chain transfer is occurring with these compounds. However, thiophene retards the rate strongly and anisole relatively weakly.

This method provides a sensitive means of studying the effect of different alkyl groups in mono- and higher substituted alkyl benzenes on the reactivity toward an ion pair of the general type involved in the Friedel–Crafts reaction. Where possible, such results could be compared with published data concerning complex formation with electrophilic species[4,5,6] and relative rates of halogenation.[7,8]

Other related problems are under investigation using this general experimental procedure.

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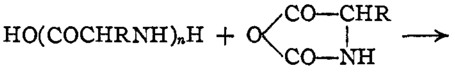
RECEIVED SEPTEMBER 23, 1953

THE MECHANISM OF POLYMERIZATION OF N-CARBOXY-α-AMINO ACID ANHYDRIDES

Sir:

The polymerization of N-carboxy-α-amino acid anhydrides (I) is believed to proceed according to reaction (1).[1,2] It was assumed, by analogy with



I

$$\mathrm{HO(COCHRNH)_nCOCHRNH_2 + CO_2} \qquad (1)$$

the polymerization of ethylene oxide, that no termination reaction occurs, and that propagation proceeds by the addition of I to the terminal free amino group present in each polypeptide chain. Water-initiated polymerizations should therefore lead to polypeptides with equal numbers of amino and carboxyl terminal groups, while amine-initiated polymers should contain amino, but no carboxyl terminal groups. Furthermore, it should be possible to prepare poly-α-amino acids of very high molecular weight.

The fact that the N-carbonyl group of I reacts to a certain extent with sodium methoxide,[3] suggested to us that reaction (2), which constitutes a *termination* reaction, should also occur. Termina-

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[2] This was done in order to keep the dielectric of the medium approximately constant, since the aromatic hydrocarbons in the table all have dielectric constants close to that of carbon tetrachloride. In the case of *p*-chloroanisole, this procedure may have permitted a significant variation in solvent dielectric; for anisole and thiophene the concentrations employed were small (<0.025 *M*) and the dielectric was probably not appreciably affected.

[3] D. C. Pepper, *J. Polymer Sci.*, **7**, 347 (1951).

[4] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **71**, 3644 (1949).

[5] D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[6] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

[7] P. B. D. De la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

[8] E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949).

[1] S. G. Waley and J. Watson, *Proc. Roy. Soc.* (*London*), **A199**, 499 (1949).

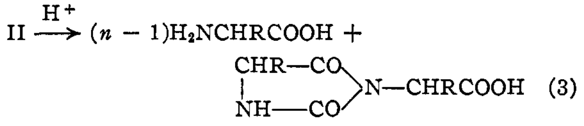
[2] L. Gold, *J. Chem. Phys.*, **21**, 1190 (1953).

[3] A. Berger, M. Sela and E. Katchalski, *Anal. Chem.*, **25**, 1154 (1953).

$$\mathrm{HO(COCHRNH)_nH + I \longrightarrow HO(COCHRNH)_nCONHCHRCOOH} \quad (2)$$

II

tion of polymerization takes place when the amino group of a growing peptide chain reacts with carbon 2 of I, leading to an urea derivative (II), with the formation of a free carboxyl group. The presence of II (R = $CH_2C_6H_5$) in poly-DL-phenylalanine (prepared by bulk polymerization of I, R = $CH_2C_6H_5$, *cf.* substance 1 in the table) was demonstrated as follows: The polymer was hydrolyzed in acetic acid–hydrochloric acid and 5-benzylhydantoin-3-β-phenylpropionic acid[4] (III, R = $CH_2C_6H_5$) was separated from DL-phenylalanine by ether extraction. Both the racemic and *meso* forms of III were isolated (30 mg. from 1.5 g. of polymer) and identified by mixed melting points with authentic samples.



$$\mathrm{II} \xrightarrow{H^+} (n-1)\mathrm{H_2NCHRCOOH} + \mathrm{III} \quad (3)$$

III

Since the polypeptides contain both terminated and unterminated chains, an excess of carboxyl groups is to be expected. The number average degree of polymerization should therefore be calculated from the total number of end groups (*i.e.*, both carboxyl and amino groups), present in the polymer.[5] We have found that the terminal amino and carboxyl groups of poly-α-amino acids can be determined by titration in anhydrous dimethylformamide with perchloric acid and sodium methoxide respectively, using thymol blue as an indicator. Results are summarized in the table.

TABLE I

Poly-α-amino[a] acid	Number of terminal groups per amino acid residue COOH (titr.) (A)	NH₂ (titr.) (B)	NH₂ (Van Slyke) (C)	Calcd. degree of polymerization $\frac{1}{C}$	$\frac{2}{A+B}$
1[b]	0.033	0.011	0.010	100	45
2[c]	.048	.017	.014	72	31
3[d]	.118	.059	.059	17	11
4[d]	.091	.020	.019	53	18
5[d]	.072	.016	.016	63	23
6[d]	.056	.016	.012	83	28
7[e]	.143	.012	.010	100	7[f]

[a] Methods of preparation *cf.* E. Katchalski, *Advances in Protein Chemistry*, 6, 123 (1951.) [b] Poly-DL-phenylalanine. [c] Poly-δ,N-carbobenzoxy-DL-ornithine. [d] Poly-ε,Nc-arbobenzoxy-L-lysine (different samples). [e] Poly-β,N-carbobenzoxy-DL-α,β-diaminopropionic acid (polymerization in anhydrous dioxane initiated by diethylamine). [f] Calculated from 1/A + B.

There is fairly good agreement between the amino group titration and the Van Slyke analysis. The table clearly illustrates the considerable excess of carboxyl groups over amino groups in the polypeptides investigated. This fact, as well as the presence of carboxyl groups in amine-initiated polymers,[6] and the relatively low molecular weight of the polymerization products, are readily explained by the termination reaction.

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[4] F. Wessely and M. John, *Z. physiol. Chem.*, **170**, 98, 167 (1927); F. Wessely, K. Schlögl and G. Korger, *Monatsh.*, **83**, 1156 (1952).

[5] The corrected degrees of polymerization appear in column 6 of the Table. Hitherto the values appearing in column 5 of the table were considered to represent the average degree of polymerization.

[6] J. H. Fessler and A. G. Ogston, *Trans. Faraday Soc.*, **47**, 667 (1951).

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DIRECT INTERACTION BETWEEN METAL ATOMS IN THE CRYSTALS OF BIS-(DIMETHYLGLYOXIME)-NICKEL(II) AND -PLATINUM(II)

Sir:

Previously the present writers have studied the dichroism of the crystals of Magnus green salt,[1,2] its related compounds,[2] and salts of tetracyanoplatinate(II),[3] and arrived at the conclusion that in the above crystals there exists a direct interaction between central platinum atoms of the planar complexes. Recently Godycki and Rundle[4] reported on the crystal structure of bis-(dimethylglyoxime)-nickel(II), suggesting the existence of a similar, though weak, interaction between nickel atoms. They have mentioned of the pleochroism of the nickel compound, but have not given any value for absorption coefficients. Moreover, their description on the pleochroism contradicts our results, though the conclusion reached agrees with ours. In this letter we wish to report on the results of the quantitative dichroism measurement, demonstrating the non-existence of the metal–metal interaction in the crystal of bis-(dimethylglyoxime)-copper and the possible existence of the metal–metal interaction in the crystals of bis-(dimethylglyoxime)-nickel(II) and -platinum(II).

Quantitative dichroism measurement by Tsuchida–Kobayashi's microscopic method[5] was performed with a microcrystal in the region from 2400 to 7000 Å. First, measurement was made with black prismatic crystals of bis-(dimethylglyoxime)-copper(II) (Fig. 1).[6] For the absorption band at the longest wave length region (Fig. 1), which is considered as due to transitions related to the metal–ligand linkages, a marked dichroism was observed. The following data were obtained: for || absorption,[7] $\nu = 54 \times 10^{13}$/sec. and log $\alpha = 1.91$[8]; for ⊥ absorption, $\nu = 57.6 \times 10^{13}$/sec. and log $\alpha = 1.65$. The relation on the dichroism with this compound agrees with that induced for planar complexes of an ordinary type,[5b] indicating that there exists

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[1] S. Yamada and R. Tsuchida, *J. Chem. Soc. Japan*, **70**, 44 (1949).

[2] S. Yamada, THIS JOURNAL, **73**, 1579 (1951).

[3] S. Yamada, *Bull. Chem. Soc. Japan*, **24**, 125 (1951).

[4] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 478 (1953).

[5] (a) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka, Japan, 1944, p. 180. (b) See, for example, S. Yamada, THIS JOURNAL, **73**, 1182 (1951).

[6] About the crystal structure, see S. Bezzi, E. Bua and G. Schiavinato, *Gazz. chim. ital.*, **81**, 856 (1951).

[7] || and ⊥ refer to results with polarized lights having their electric vectors parallel and perpendicular to the planes of the complexes, respectively.

[8] α denotes absorption coefficient per mm. of the crystal.