growing chain (after the first one or two units have been added to the initiator if the latter is not a preformed polymer) and suggest that the propagation reaction is essentially similar to that established for the polymerization of DL-phenylalanine and DL-leucine N-carboxy anhydrides. Similar observations have been made in nitrobenzene and N,N-dimethylformamide solutions.

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RECEIVED DECEMBER 17, 1956

POLYPEPTIDES. Xa. ADDITIONAL COMMENTS OF THE AMINE-INITIATED POLYMERIZATION

Sir:

The foregoing communication by Ballard and Bamford[1] disputes our finding of two successive propagation constants in the polymerization of γ-benzyl-L-glutamate N-carboxy-anhydride and thereby casts doubt on the identification we had made of the first, relatively slow propagation with the randomly coiled configuration and the second, faster propagation with the α-helical configuration which is attained by each growing chain when it passes a critical chain length.[2]

In each case the interpretations are consistent with the kinetic data reported: it is the data that differ so much in the two investigations. As a consequence the course of the polymerization must be quite different as well. It is our contention that our N-carboxy anhydride was in such a state of purity that the polymerization consists simply of a rapid initiation followed by chain growth characterized by two successive propagation constants, the second taking over from the first when the chain reaches a length of about eight.

Since there is no indication that Ballard and Bamford[1] have followed precisely the procedure of anhydride preparation and purification[3] we employed, their failure to reproduce our results is not surprising inasmuch as the kinetic effect we have isolated is easily suppressed. On the other hand, we have observed the behavior they report with relatively unpurified anhydride. Since upon sufficient recrystallization the behavior we have reported was always found we have naturally concentrated our attention on what appeared to be the purer and more reproducible anhydride. Although this work is reported in detail in forthcoming papers,[4,5] two particularly relevant points deserve mention here.

(1) If the N-carboxy anhydride is used after its first crystallization a linear first-order behavior similar to that of Ballard and Bamford[1] is observed throughout the polymerization (A in Fig. 1). However, after one recrystallization from methylene dichloride the two successive propagations are clearly evident (B in Fig. 1). Since the HCl content of the unrecrystallized anhydride was 1.0 mole % and since this could react with the initiator, n-hexylamine, to produce a possibly "active" impurity, we

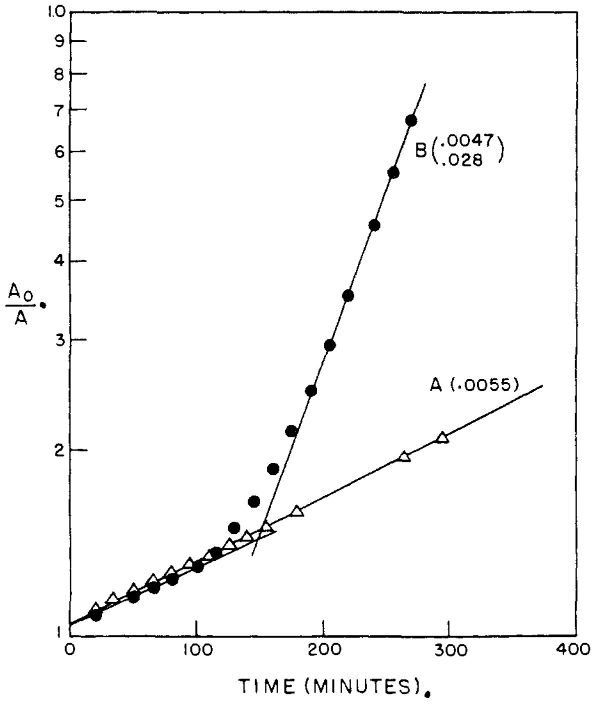

Fig. 1.—Polymerization of γ-benzyl-L-glutamate N-carboxy anhydride initiated with n-hexylamine ([A]/[I] = 20) in dioxane solution at concentration of 4 g./100 cc. at 25.0°. Case A corresponds to impure anhydride and case B to the same anhydride after one recrystallization.

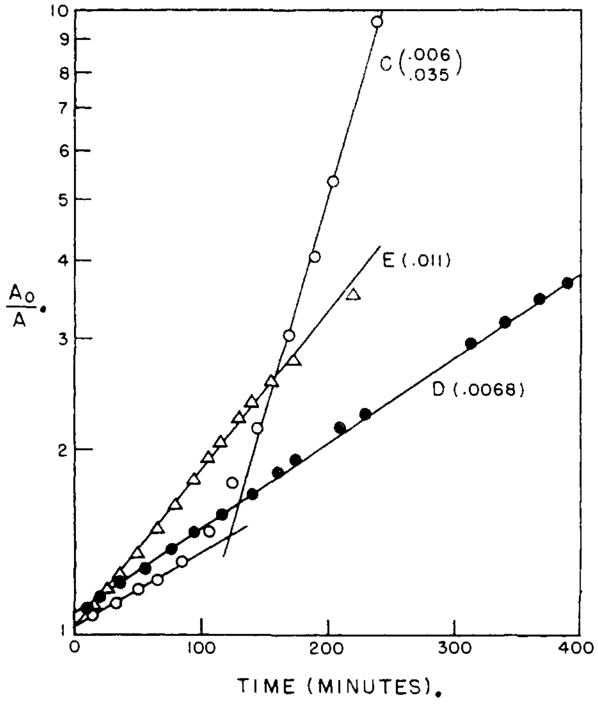

Fig. 2.—Polymerization under same conditions as Fig. 1. Case C is a highly purified anhydride (HCl < 0.1 mole %). Cases D and E correspond to the addition of n-hexylamine hydrochloride to the extent of 0.67 and 5.0 mole %, respectively.

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[1] D. G. H. Ballard and C. G. Bamford, THIS JOURNAL, **79**, 2336 (1957).

[2] P. Doty and R. D. Lundberg, *ibid.*, **78**, 4810 (1956).

[3] E. R. Blout and R. H. Karlson, *ibid.*, **78**, 941 (1956).

[4] R. D. Lundberg and P. Doty, *ibid.*, in press (1957).

[5] E. R. Blout and M. Idelson, *ibid.*, in press (1957).

carried out polymerizations with a highly purified anhydride[5] (C in Fig. 2) to which 0.67 and 5.0 mole % of *n*-hexylamine hydrochloride had been added (D and E in Fig. 2). The results show that this adduct eliminates the second propagation step and produces pseudo first-order reactions which bracket the one reported by Ballard and Bamford[1] as "the most reliable thus far obtained." It is evident, therefore, that the results of Ballard and Bamford can be reproduced by impure anhydride or by the addition to highly purified anhydride of one of the impurities removed during its purification. Thus, the sensitivity of this effect to contamination of the anhydride suggests that the presence of *some* impurity is the most likely explanation of their results. Space prevents taking up other possibilities that could arise from not carrying out the purification of the anhydride at −30° as described.[5] Moreover, the premise of Ballard and Bamford concerning the uniqueness of the sublimation in anhydride purification appears invalid inasmuch as we have observed the two successive propagation steps to be even more dramatically exhibited in L-leucine N-carboxy anhydride, both before and after sublimation of the product purified as described.[5] Consequently, we cannot concede that Ballard and Bamford's failure to observe the reported kinetic effect is evidence against its existence.

(2) The kinetic effect we have reported must, of course, be reflected in the molecular weight distribution of the product. In this case, the distribution must be exceedingly broad as we have reported.[2] In case C, for example, the number average DP is 20 and the weight average DP is 170.[6] If, on the other hand, the second propagation step is suppressed as in Case D, the distribution should narrow. This is indeed observed: for case D, $DP_w = 46$, $DP_N = 17.5$. The analysis of the products, therefore, is seen to support the original contention that two successive rate constants are observed under the conditions reported.

We wish to thank Dr. E. R. Blout for his very helpful collaboration in this work.

[6] These measurements were made by Mr. J. C. Mitchell in this Laboratory using the Archibald approach-to-equilibrium technique in ultracentrifugation.

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RECEIVED FEBRUARY 1, 1957

AN ALLEGED FREE RADICAL REACTION IN WHICH BENZENE UNDERGOES ATTACK MORE READILY THAN NITROBENZENE

Sir:

Wieland and Meyer[1] reported that the reaction of triphenylmethyl radical with aromatic substrates, in the presence of benzoyl peroxide, afforded *para*-substituted tetraphenylmethanes. The discovery[2] that these substances were, in reality, *meta* isomers, prompted us to reinvestigate the reaction.

Although nitrobenzene as a substrate was not studied in the original Wieland[1] work, it seemed of special interest to us because of its propensity to participate in free radical reactions with greater ease than benzene itself ($C_6H_5NO_2/C_6H_6)K = 4$).[3]

We found that when triphenylmethyl radicals (in the presence of benzoyl peroxide) were permitted to compete for benzene and nitrobenzene (equimolar mixture) the only products that could be detected were tetraphenylmethane (10%) and *p*-bis-triphenylmethylbenzene, m.p. 330° (9%). (The latter was identical in m.p. and infrared spectrum with material prepared by an independent synthesis.) Both infrared analysis of the crude reaction product and C^{14}-tracer experiments confirmed that nitrotetraphenylmethanes were formed only in trace amounts, if indeed at all.

In conjunction with this work, it was also found that triphenylmethyl radical is not consumed to any appreciable extent by reaction with the nitro function of nitrobenzene in the *absence* of benzoyl peroxide. This is in contradiction to the report by Hammond and Ravve[4] that a quantitative reaction occurs, to afford triphenylcarbinol, azobenzene and phenol among other products.

After a benzene solution of triphenylmethyl (prepared in benzene from triphenylmethyl chloride and mercury) and nitrobenzene had been exposed to diffuse daylight for 24 hours, practically all of the triphenylmethyl was still present and infrared analysis showed the complete absence of azobenzene. Trace amounts of phenol could be detected after a reaction period of 4 days, but its formation was independent of the presence of nitrobenzene since it was also found in mixtures containing only triphenylmethyl and benzene.

The formation of phenol might reasonably be explained by assuming that phenyl radicals are produced in some manner, as postulated by Hammond and Ravve, but the implication[4] that these radicals then abstract oxygen from nitrobenzene appears to be invalid. The presence of trace amounts of atmospheric oxygen seems to afford a better explanation for the phenol production.

We are currently investigating the cause of the surprising reversal of relative reactivity of trityl radicals toward benzene and nitrobenzene. Several possibilities occur to us at this time. (1) Perhaps the Wieland reaction, which has been traditionally considered free radical in nature is instead ionic. (2) The trityl radical may have some carbonium ion character due to the I effects of the three phenyl groups.[5] (3) An ion-pair type complex might form rapidly and reversibly between the easily oxidized trityl radical and nitrobenzene, thus vitiating normal trityl radical attack on that nucleus.

While the first of these explanations cannot be dismissed at this time, it does not seem like an attractive possibility. The Baeyer–Villiger reaction,[6] which almost certainly proceeds *via* a tritylcarbonium ion, occurs only with activated nuclei. Even toluene does not react in a four day period.[2] The

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[1] H. Wieland and A. Meyer, *Ann.*, **551**, 249 (1942).

[2] R. A. Benkeser and R. Gosnell, THIS JOURNAL, **78**, 4914 (1956).

[3] D. H. Hey, *et al.*, *J. Chem. Soc.*, 2094 (1952).

[4] G. S. Hammond and A. Ravve, THIS JOURNAL, **73**, 1891 (1951).

[5] See R. L. Dannley and M. Sternfeld, *ibid.*, **76**, 4543 (1954), where this general concept was proposed.

[6] A. Baeyer and V. Villiger, *Ber.*, **35**, 3018 (1902).