A Novel Synthesis of AB-Aromatic Polyamides from Aromatic Amino Acids and Carbon Disulfide

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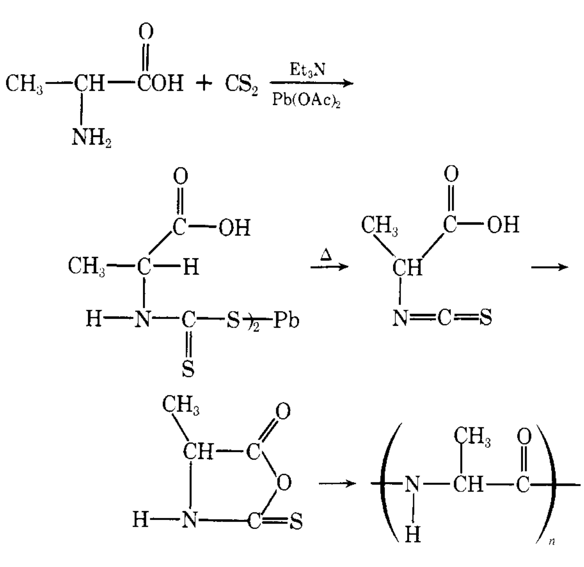
ABSTRACT: High molecular weight poly-*p*-benzamide has been prepared by a novel two-stage reaction involving: (1) reaction of *p*-aminobenzoic acid with carbon disulfide using pyridine as catalyst in aromatic solvents (nitrobenzene, chlorobenzene, and *o*-dichlorobenzene) to give an oligomeric precursor of poly-*p*-benzamide containing carboxyl and isothiocyanate ends; and (2) *solid state* thermal polymerization of the oligomer to high molecular weight polymer (η_{inh}'s to 4.76). The synthesis of high molecular weight polymer here is in contrast to the reported preparation of *N,N'*-di-*p*-carboxyphenylthiourea in high yield (92%) by reaction of *p*-aminobenzoic acid with CS_2 (used also as solvent) with pyridine and iodine as H_2S acceptors. The polymer prepared in this work was found soluble in sulfuric acid. Tough films and fibers were prepared from H_2SO_4 solutions of the polymer. The reaction has been also extended to the synthesis of poly-*m*-benzamide.

Dehydration of aromatic amino acids by thermal means has generally led to low molecular weight polymer. For example, when heated alone at >200 °C, *p*-aminobenzoic acid decarboxylates to a high yield of aniline and low yield of low molecular weight polymer.[1] Simple esters such as methyl 4-aminobenzoate have been found also to yield only low molecular weight polymer.[1] Thermal condensation of 4-acetamidobenzoic acid at 300 °C has been reported to yield polymer, but unfortunately, the properties were not given.[2] However, the preparation of moderately high molecular weight poly-*p*-benzamide has been reported by several authors. A recent paper by Iwakura et al.[3] reports the preparation of poly-*p*-benzamide with η_{inh} – 1.5 (in H_2SO_4) in 100% yield via the thermal polymerization (at 300–350 °C) of *p*-(*p*-phenoxycarbonylaminobenzamide)benzoic acid. Two low-temperature synthetic routes to poly-*p*-benzamide have been reported. They involve polymerization of thionylaminobenzoyl chloride and 4-aminobenzoyl chloride hydrochloride, respectively. In the former case just enough water or LiOH is added to an amide solution (containing LiCl for solubilizing polymer) of the thionylaminobenzoyl chloride to remove the thionyl group. In this way polymer with η_{inh} up to 1.47 (in H_2SO_4) has been prepared by Schaefgen et al.[4] Lower molecular weight ($\eta_{inh} \sim 0.3$) polymer by essentially the same chemistry has been reported by Shtil'man et al.[5] In their work, however, no mention was made of using a lithium base or LiCl which could explain the lower molecular weight obtained. In the case of 4-aminobenzoyl chloride hydrochloride, Preston[6] has reported preparation of poly-*p*-benzamide with η_{inh} of 0.76 in dioxane–pyridine (1:1 by volume).

The present paper deals with the polycondensation of *m*- and *p*-aminobenzoic acid using carbon disulfide. Polyalanine has been reported[7] to have been prepared in 80% yield via reaction sequence 1 below which involves carbon disulfide as a condensing agent.



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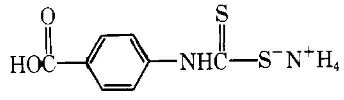
p-Aminobenzoic acid has been reported to react with carbon disulfide under basic conditions to give an ammonium salt (I).[8] It was felt under the right conditions a salt of the type I might eliminate the elements of H_2S to give *p*-carboxyphenyl isothiocyanate (II) which would self condense to the *N*-thiocarboanhydride (III) which in turn would eliminate carbon oxysulfide and give poly-*p*-benzamide (IV) (reaction sequence 2) in a way analogous to alanine above. The key to success of such a sequence would be the capture of the isothiocyanate group by the carboxyl before it reacts with *p*-aminobenzoic acid to give *N,N*-di-*p*-carboxyphenylthiourea (V). The latter compound was obtained in 92% yield by Fry[9] when *p*-aminobenzoic acid was treated with carbon disulfide and pyridine in the presence of I_2 (aids H_2S removal by the reaction: $H_2S + I_2 \rightarrow 2HI + S$). The same reaction in the absence of I_2 has not been reported. Fry reported, however, that electron withdrawing substituents such as *m*-nitro and *m*-chloro exerted an unfavorable effect upon the reaction giving only trace and 29.8% yields, respectively, of the corresponding thiocarbanilide in the absence of I_2. On the other hand, when the same reactions were carried out in the presence of I_2 the yields were



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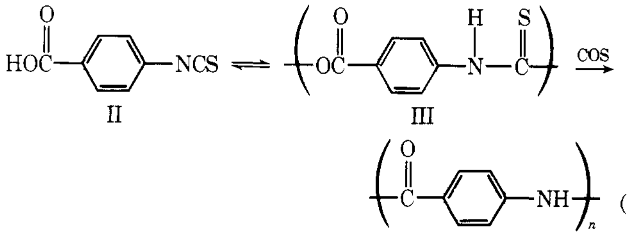

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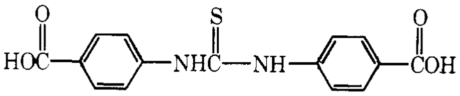

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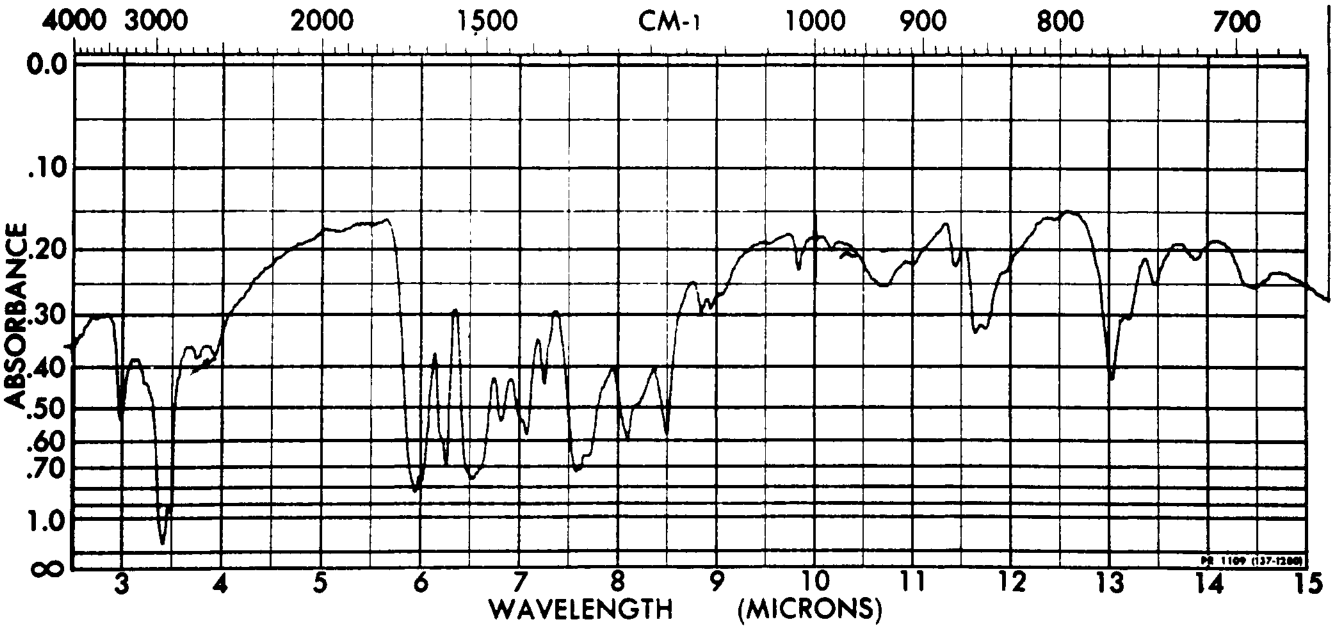

Figure 1. Infrared spectrum ("Nujol" mull) of oligomer from *p*-aminobenzoic acid and carbon disulfide.

Table I
Reaction of *p*-Aminobenzoic Acid with Carbon Disulfide

Entry	PABA, mol	CS$_2$,[a] mol	PyN, mol	Solvent	Vol of solvent, ml	Reaction time–temp profile, hr (°C)	Yield[b] solid, g	Elemental anal. C, H, N, S
A	1.0	5.2	1.0	PhNO$_2$	1500	0 (RT) 0.33 (54) 2.6 (87) 6.2 (115) 7.2 (133)	15	58.8, 4.48, 9.13, 6.64
B	(Filtrate from entry A)					0 (RT) 0.25 (98) 0.45 (145) 0.92 (162) 1.9 (150) 2.9 (188)	28	60.6, 4.28, 9.65, 0.93
C	0.10	0.52	0.10	PhNO$_2$	100	0 (RT) 0.83 (95) 1.27 (128) 3.0 (172) 4.26 (172)	7[c]	
D	0.10	0.52	0.10	PhNO$_2$	200	0 (RT) 0.83 (120) 1.27 (154) 3.0 (170)	1.5	
E	0.10	0.52	0.40	PhNO$_2$	200	5.0 (110–160)	4.0	
F	0.36	0.73	0.37	PhNO$_2$	550	25.6 (117+)	36	
G	0.10	0.52	0.40	PhCl	200	96 (reflux)	0.34	
H	0.10	0.52	0.40	*o*-DClPh	200	24 (reflux)	0.39	

[a] Much of the carbon disulfide was lost by evaporation during reflux. [b] Product was isolated by suction filtration and was dried in a ~80 °C vacuum oven. [c] 0.044 mol of unreacted *p*-aminobenzoic acid (identified by ir spectrum) was recovered by evaporation of solvent–CS$_2$–PyN from filtrate on a rotary evaporator.

high, 88 and 90%, respectively. The nature of retardation in the absence of I$_2$ may well have been the tying up of the amino group by H$_2$S and thereby lowering its reactivity toward the isothiocyanate formed in situ. If this hypothesis is correct, the reaction involving *p*-aminobenzoic acid in the absence of I$_2$ could take a different course that involves reaction of the carboxyl group with the isothiocyanate formed in situ as shown in reaction sequence 2.

Experimental Section

Preparation of Oligomer. To a solution of 31.6 g (0.40 mol) of pyridine and 39.5 g (0.52 mol) of carbon disulfide in 200 ml of nitrobenzene contained in a 500-ml three-necked flask with a 2-ft Allihn condenser, drying tube, mechanical stirrer, and N$_2$ purge was added 13.7 g (0.1 mol) of *p*-aminobenzoic acid. As the reaction mixture was warmed with mantle, a clear orange solution was obtained. The reaction was heated rapidly to 110 °C then more slowly to 160 °C. Much of the CS$_2$ was lost through evaporation during heating. After ~2 hr the reaction became cloudy and gave subsequently a yellow precipitate. After heating for a total of 5 hr the mixture was allowed to cool to below 100 °C and filtered by suction through a Buchner funnel. The filter cake was washed with toluene and air dried on filter. A 4-g yield of light yellow solid was collected whose ir spectrum appears in Figure 1. The ir spectrum along with elemental analyses on other runs (see Table I, entries A and B) indicate this material to be an oligomer of poly-*p*-benzamide. In a separate run 44% of the *p*-aminobenzoic acid was recovered by evaporation of the filtrate to dryness.

Preparation of Poly-*p*-benzamide. To a 25-mm o.d. polymer tube was added 1.0 g of the above oligomer. Air was removed from

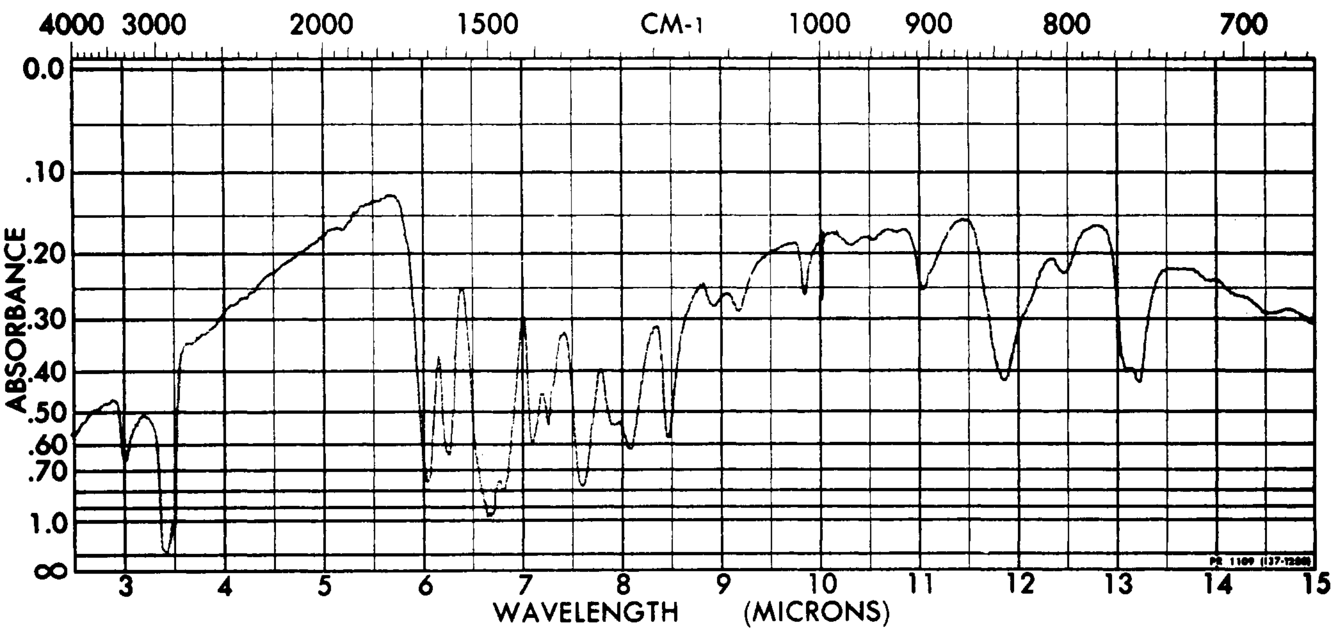

Figure 2. Infrared spectrum ("Nujol" mull) of poly-*p*-benzamide from *p*-aminobenzoic acid and carbon disulfide.

the tube by alternately purging with N_2 and evacuating. The tube was then heated under N_2 in an oil bath for 1 hr at 180–182 °C, 0.25 hr at 240–244 °C, and 1 hr at 256 °C followed by heating 1 hr at 400 °C. The yield was 0.6 g of a light yellow solid whose ir spectrum appears in Figure 2 which is identical with that of polymer from *p*-aminobenzoyl chloride hydrochloride. The η_{inh} was 4.76 (0.5 g/dl concentrated H_2SO_4 at 30 °C).

Anal. Calcd for C_7H_5NO: C, 70.5; H, 4.23; N, 11.8. Found: C, 70.16, 70.26; H, 4.77, 4.80; N, 11.3, 11.4; S, 0.35, 0.36.

Mass Spectroscopy of Off Gases from Oligomer. A sample of oligomer was heated (2 °C/msec) in helium and held for 2 sec in separate experiments at 350 and 400 °C on a platinum ribbon of a Du Pont Model 21-492 high-resolution mass spectrometer. The results were qualitatively similar at both temperatures. Masses corresponding to large amounts of COS, CS_2, H_2S, pyridine, and nitrobenzene were identified along with smaller but significant quantities of CO_2, water, and phenyl isocyanate.

Results and Discussion

Poly-*p*-benzamide has been prepared in high molecular weight by a two-stage reaction involving: (1) reaction of *p*-aminobenzoic acid with carbon disulfide using pyridine as catalyst in aromatic solvents (nitrobenzene, chlorobenzene, and *o*-dichlorobenzene) to give an oligomeric precursor (IX) (see reaction sequence 3 below); and (2) *solid state* polymerization of IX to high molecular weight poly-*p*-benzamide.

Although reaction scheme 3 seems most plausible for the formation of high molecular weight polymer, *N,N'*-di-*p*-carboxyphenylthiourea (V) as a reactive intermediate cannot be ruled out. *N,N'*-Diphenylthiourea has been reported to react with benzoic acid to give a 93% yield of benzanilide.[10] Likewise, V may be envisioned to react with *p*-aminobenzoic acid to give an amide dimer which could serve as a site for polyamide chain growth.

Table I exhibits reaction conditions for formation of the prepolymer (IX). In each case (entry A–H) the reaction mixture was initially a homogeneous clear solution which after refluxing for a period of time became cloudy with subsequent formation of a precipitate. The precipitate in each case was found to be an oligomer best described as IX. Figure 1 represents a typical ir spectrum of the product and is consistent with IX although no band is clearly assignable to the —N═C═S group. This might be explained by the condensation of this group to *N*-thiocarboanhydride. Assignments of other absorption maxima to functionalities are as follows: 3.0 μ (amide NH stretching vibration); 3.75 and 3.92 μ (carboxyl OH stretching vibration); 5.95 μ (carboxyl

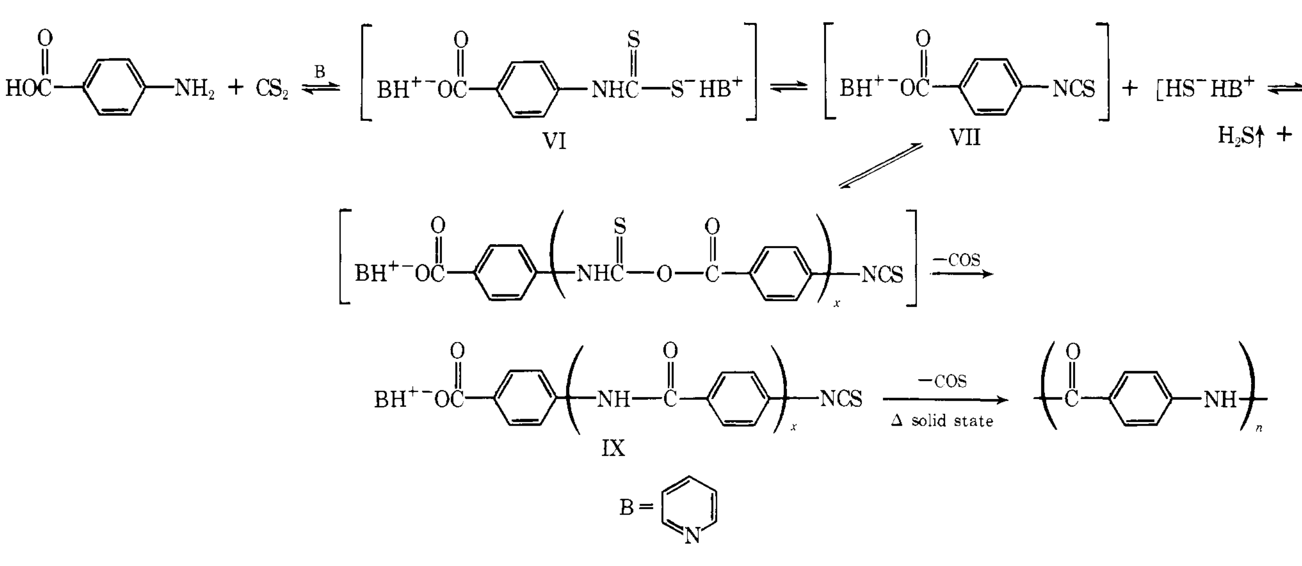

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Table II
Preparation of Poly-*p*-benzamide[a]

Entry	Precursor used from Table I	Wt of Precursor used, g	Agitation	Pressure N_2 atm, mm	Temp of vapor bath, °C[b]	Time at given temp, hr	Yield of polymer, g[d]	Elemental anal.		η_{inh}[e] (H_2SO_4)	Polymer color
								Calcd (C_7H_5NO)	Found		
I	E	2.0	Paddle Stirrer	Positive N_2	130	1.0					
					250	1.0				0.06	
					300	1.0				0.28	Lt yellow
					400	0.25	1.2			2.16	
J	E	1.0	None	Positive N_2	180–182	1.0					
					240–244	0.25					
					256	1.0					
					400	1.0	0.60	C 70.5	70.2	4.76	Lt yellow
								H 4.23	4.8		
								N 11.8	11.3		
								S 0	0.36		
K	D	3.0	Paddle Stirrer	10	130	1.0					
					250	1.0					
					300	1.0					
					400	0.5				3.4	Lt yellow
L	F	20	None	7–8	191[c]	0.5					
					203	0.5					
					295	1.0					
					395	0.75	12.2 (0.86)			1.62	Brown

[a] Polymerizations were conducted in polymer tubes or wide mouth tubes equipped with paddle type stirrers (when indicated), N_2 bleed, and vacuum line. [b] Temperature monitored using Leeds-Northorpe "8690" Millivolt Potentiometer with iron constantan thermocouple. [c] Temperature of sample. [d] Small amount of sublimate (in parentheses) collected from above body of the reaction. [e] η_{inh}, the inherent viscosity is $[\ln \eta_{rel}]/C$ at 30 °C in concentrated H_2SO_4 where C is the polymer concentration (0.5 g/100 ml).

CO); and 6.03 μ (amide I CO). Absorption at 7.5 μ (urea C=S)[11] is absent indicating little or no *N,N'*-di-*p*-carboxyphenylthiourea (V). The inherent viscosities of the oligomeric products range between 0.06 and 0.08, except for entry B which may be higher because of the higher reaction temperature employed. The low sulfur analysis for entry B is consistent with a higher molecular weight and the DP may be as high as 30 based on S analysis. The reaction appears to proceed quite cleanly with the filtrate yielding only unreacted *p*-aminobenzoic acid (see entry C). Overall, 80% of the *p*-aminobenzoic acid can be accounted for in entry C, including that which was recovered and which was converted via IX to high polymer (see discussion below). Of the three solvents tried, nitrobenzene gave the highest yields of IX (compare entries G and H with A–F).

Reaction conditions for the conversion of IX to high molecular weight poly-*p*-benzamide are given in Table II. Carbon oxysulfide was identified as a reaction product by mass spectroscopy at both 350 and 450 °C. Appreciable amounts of pyridine, CS_2, H_2S, and nitrobenzene were also evolved. To achieve very high molecular weight polymer without causing deleterious side reactions (cross-linking or branching), it was necessary to build up sufficient molecular weight at moderately high temperatures (to 300 °C) so that exposure to very high temperatures (to 400 °C) could be kept short. The very high temperatures employed were required to bring about sufficient chain mobility in the solid state polymerization to get condensation of ends. Results under atmospheric N_2 and reduced pressure were similar. The polymer was identified by ir and elemental analysis (entry J). The ir spectrum exhibited in Figure 2 is identical with that of poly-*p*-benzamide prepared from *p*-aminobenzoyl chloride hydrochloride. The small amount of S (0.36%) in the polymer may be present in the form of thiourea linkages or residual *N*-thiocarboanhydride linkages. No thioamide linkages are expected since it is well established that in aromatic *N*-carboanhydrides, and presumably *N*-thiocarboanhydrides, the carbon atom which is eliminated as CO_2 (COS in case of *N*-thiocarboanhydrides) is the one attached to nitrogen and not to the ring.[12,13] The mass conversion of precursor IX to high molecular weight poly-*p*-benzamide in each case was about 60% (in each case a sublimate collected above the body of the reaction which was not identified). In the case of Entry C (Table I), a 60% mass conversion represents a 34% conversion of *p*-aminobenzoic acid to poly-*p*-benzamide, 44% being recovered from the filtrate. Sublimation during polymerization accounts for much of the remainder of the *p*-aminobenzoic acid.

The poly-*p*-benzamide prepared by the above method was soluble in 100% H_2SO_4. Tough films were wet cast and fibers wet spun into water from H_2SO_4 solutions of polymers listed in Table II. Once the crystallinity had been destroyed by dissolving the polymer in H_2SO_4, the isolated polymer was found soluble in dimethylacetamide containing LiCl, indicative of a very low level of cross-links and branches.

The reaction described above for *p*-aminobenzoic acid was extended to *m*-aminobenzoic acid using similar conditions. The oligomer with an η_{inh} of 0.08 was heated as follows: 1 hr/250 °C; 1 hr/300 °C; and 15 min at 400 °C. The overall polymer yield was 25% (based on *m*-aminobenzoic acid) and the η_{inh} was 0.62. The polymer was identified by its ir spectrum.

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(13) A 56% yield of benzanilide was prepared by the author from phenyl isothiocyanate and benzoic acid in nitrobenzene with pyridine catalyst. Surprisingly, this reaction was not found during a cursory literature survey.

A New Derivation of Average Molecular Weights of Nonlinear Polymers

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ABSTRACT: A new method for calculating average molecular weights is presented for nonlinear polymers. In contrast to the previous methods of Flory and Stockmayer which first calculate the distribution of all species and then use the distributions to calculate average properties, the new method calculates these properties directly. In contrast to the method of Gordon, probability generating functions are not required. Starting with elementary probability and utilizing the recursive nature of network polymers, property relations can be developed more simply. We illustrate the method for calculations of $\bar{M}_w$, $\bar{M}_z$, and the gel point for a wide variety of polyfunctional polymerizations.

Flory[2] and Stockmayer[3] laid out the basic relations between extent of reaction and resulting structure in nonlinear polymerizations. Starting with the assumptions of equal reactivity of functional groups and no intramolecular reactions, they used combinatorial arguments to derive expressions for the size distribution of the finite molecules as a function of reaction extent. For cases of practical importance these distribution functions become quite complex (e.g., Stockmayer[4]).

At present, experimentally we can only measure average molecular weights of nonlinear polymers. It is possible, though algebraically very tedious, to calculate these averages from the distribution functions. General treatment of nonidealities such as intramolecular reactions or ring formation using distribution functions appears to be prohibitive.

Gordon[5] showed that the molecular weight averages could be calculated directly using the theory of stochastic branching processes.[6] He and coworkers have used this theory extensively on nonlinear polymer problems.[7-10] Gordon's technique involves abstract mathematics and requires deriving probability generating functions. The method is quite general but rather difficult to use.

Our interest in developing mathematical models for network polymer processing motivated us to seek simpler relations which could readily be incorporated into a larger, complex process model. Below we describe a new, simpler method for deriving average properties of nonlinear polymers.

We retain Flory's three simplifying assumptions, namely:
(1) all functional groups of the same type are equally reactive;
(2) all groups react independently of one another;
(3) no intramolecular reactions occur in finite species.
(Some departures from these assumptions, such as unequal reactivity and substitution effects and some aspects of intramolecular loops, can also be treated with our method.[11])

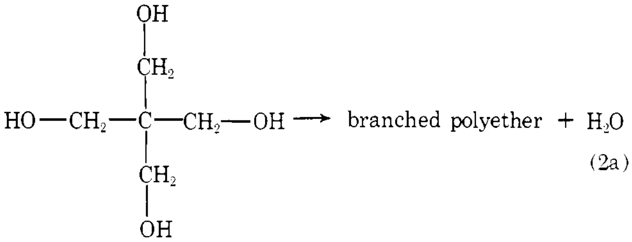
Our method uses the recursive nature of the branching process and an elementary law of conditional expectation. Let A be an event and $\bar{A}$ its complement. Let Y be a random variable, $E(Y)$ its expectation (or average value), and $E(Y|A)$ its conditional expectation given the event A has occurred. Then the *law of total probability for expectations* is

$$E(Y) = E(Y|A)P(A) + E(Y|\bar{A})P(\bar{A}) \qquad (1)$$

This law is discussed in most texts on probability theory.[12]

Stepwise Polymerizations

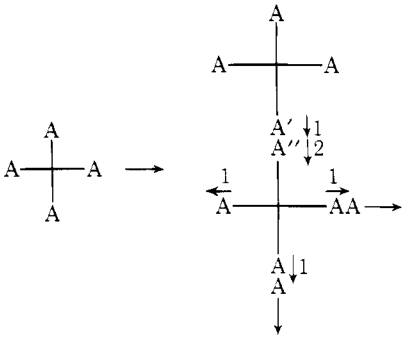
$\bar{M}_w$ for Homopolymers. Let us first illustrate the method with some simple examples. Consider the simplest case, the one treated by Flory,[2] the reaction between similar f functional molecules. An example is the etherification of pentaerythritol:



$$HO{-}CH_2{-}C(CH_2OH)_2{-}CH_2{-}OH \longrightarrow \text{branched polyether} + H_2O$$

(2a)

First we will only consider stepwise or condensation polymerizations, ignoring the effects of any condensation products for the moment. A later section treats chainwise or addition polymerizations. We can schematically represent the polymerization of A_f moles of monomer bearing f groups by



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