# Condensation Reaction between Chain Ends of Poly(p-benzamide)

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ABSTRACT:    It has been proved experimentally that the condensation reaction be-
tween chain ends of poly(p-benzamide), (PBA), takes place and that the degree of
polymerization (DP) of PBA increases by annealing in both the solid and liquid-
crystalline states. A theoretical analysis of the reaction has shown that the DP dis-
tribution of the resultant polymer is again the most probable and the conversion of
the reaction by weight is fairly high. The reactivity of PBA in the solid-crystalline
state exceeded that in the liquid-crystalline state.
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    Crystal / Most Probable Distribution / Annealing / Dimethylacetamide /

Poly(p-benzamide), (PBA), which is one of
the aromatic polyamides consisting of long, rigid
and rodlike molecules, is known to form liquid
crystals in solution. By spinning these liquid
crystals into a coagulation bath, one can make
high modulus and high temperature-resistant
fibers with high degree of orientation and crys-
tallinity.[1] This polymer can be produced by a
direct polycondensation reaction of p-amino-
benzoic acid by means of triphenyl phosphite
in N-methylpyrrolidone (NMP)—pyridine solu-
tion containing lithium chloride.[2] This reaction
usually results in rather low molecular weight
materials. This may be attributed to the termi-
nation of the polycondensation reaction owing
to the low solubility of aromatic polyamide.

PBA precipitates from dilute solution into
fibrous crystals in which molecular chains of
PBA seem to align, in a nematic arrangement,
along the fiber direction in view of its molecular
rigidity.[3] The liquid-crystalline phase of PBA
is regarded as nematic, where the molecules are
arranged side by side.

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Consequently, an end of a PBA molecule is
considered likely to exist close to the end of
another molecule even in the states of solid and
liquid crystals. Therefore, further condensation
reaction may occur between the chain ends at
high temperature. If this happens, obviously,
the thermal and mechanical properties of PBA
fibers would be improved. The purpose of the
present article is to examine the possibility of
the condensation reaction between the chain
ends of PBA in both the solid- and liquid-
crystalline phases.

## EXPERIMENTAL

### Preparation of Original PBA

Two samples of PBA were prepared according
to the method of Yamazaki, et al.[2] A mixture
of p-aminobenzoic acid (11 g, 0.4 mol/l) and
triphenyl phosphite (24.8 g) equimoles to the
monomer as catalyst in a mixed solvent (200 ml)
of NMP and pyridine containing LiCl (10 g)
was heated at 80°C for 6 hr with stirring under
nitrogen. The molecular weights of the resulting
polymers varied with the amounts of pyridine
in NMP. To obtain high (H-1) and low (L-1)
molecular weight samples, NMP—pyridine mix-
tures of 20-% and 80-% pyridine were used in

the reaction, respectively.

After cooling, the reaction mixture was poured into a large amount of methanol, and the precipitated polymer was isolated, ground to powder, washed well with methanol and then dried to constant weight under reduced pressure.

### Condensation Reaction of Original PBA

The condensation reaction of the PBA sample in the as-polymerized solid state prepared in the manner described above was carried out by annealing at 200°C *in vacuo* to avoid any oxidation reaction. The powder of the low molecular weight PBA sample (L–1) was put into a sealed glass tube having a branch to exclude water formed by the reaction, then kept in a silicone bath at a constant temperature for 5, 12, and 24 hr.

A liquid-crystalline PBA solution was prepared by dissolving the high molecular weight PBA sample (H–1) (7 wt%) in *N, N*-dimethylacetamide (DMAc) containing 3-wt% LiCl. Under a polarized microscope, the anisotropic liquid-crystalline phase together with transparent isotropic phase were observed in this highly viscous solution at room temperature. The condensation reaction of this liquid-crystalline solution was carried out by annealing in a sealed glass tube filled with nitrogen gas at 200°C for 3, 6, 12, and 24 hr. All of these solution samples turned into gel during thermal treatment. It was confirmed by an optical method that at 200°C the systems consisted totally of the liquid-crystalline phase. After cooling, each sample was washed well to remove all DMAc and LiCl, ground to powder and then dried *in vacuo*.

### Viscosity Measurements

Reagent grade DMAc was purified by distillation over $CaH_2$ at 68°C under reduced pressure (23 mmHg) and was used as the solvent for the viscosity measurements. Dilute solution viscosities of the L-series samples annealed in the solid-crystalline state and of the H-series ones annealed in the liquid-crystalline state were measured in DMAc containing 3 wt% of special grade LiCl at 20°C and in special grade concentrated $H_2SO_4$ (97 wt%) at 30°C, respectively, using Ubbelohde-type viscometers. Intrinsic viscosities were then determined for each sample.

### RESULTS AND DISCUSSION

The values of the intrinsic viscosities $[\eta]$ obtained for L- and H-series samples are listed as a function of annealing time in Tables I and II, respectively. Since the intrinsic viscosities of the samples increased with an increase in the annealing time, it is obvious that the condensation reaction between chain ends of PBA occurs during the annealing in both the solid- and liquid-crystalline states.

It is interesting to estimate the number of PBA molecules connected through the condensation reaction by the annealing, *i.e.*, "the degree of polymerization" of the product in terms of the original PBA molecules, the molecular weight distribution of the resultant polymer and the

**Table I.** Characteristic quantities for annealing PBA in solid-crystalline state

| Sample | Annealing time, hr | $[\eta]$ | $\bar{x}_w$ | $\bar{M}_w \times 10^{-3}$ | $q$ | $E(m)$ | Conversion |
|--------|--------------------|----------|-------------|----------------------------|-----|--------|------------|
| L–1 | 0 | 0.139 | 47 | 5.7 | 0 | 1.0 | 0 |
| L–2 | 5 | 0.162 | 52 | 6.1 | 0.079 | 1.079 | 0.15 |
| L–3 | 12 | 0.163 | 52 | 6.2 | 0.082 | 1.082 | 0.16 |
| L–4 | 24 | 0.201 | 58 | 6.9 | 0.181 | 1.181 | 0.33 |

**Table II.** Characteristic quantities for annealing PBA in liquid-crystalline state

| Sample | Annealing time, hr | $[\eta]$ | $\bar{x}_w$ | $\bar{M}_w \times 10^{-4}$ | $q$ | $E(m)$ | Conversion |
|--------|--------------------|----------|-------------|----------------------------|-----|--------|------------|
| H–1 | 0 | 1.45 | 172 | 2.05 | 0 | 1.0 | 0 |
| H–2 | 3 | 1.47 | 173 | 2.06 | 0.007 | 1.007 | 0.014 |
| H–3 | 6 | 1.49 | 175 | 2.08 | 0.015 | 1.015 | 0.030 |
| H–4 | 12 | 1.59 | 181 | 2.15 | 0.049 | 1.049 | 0.096 |
| H–5 | 24 | 1.68 | 186 | 2.22 | 0.076 | 1.076 | 0.15 |

conversion of the condensation reaction. Papkov, et al.,[4] obtained the intrinsic viscosity—molecular weight relationship for PBA in DMAc containing 3-wt% LiCl at 20°C in terms of the weight average molecular weight, $\bar{M}_w$.

$$[\eta] = 1.59 \times 10^{-8} \bar{M}_w^{1.85} \qquad (1)$$

Actually, eq 1 is valid only for the PBA samples the distribution of the degree of polymerization (DP) of which is the most probable. It is not self-evident, however, that the DP distribution of the L- and H-series samples used here is the most probable. Therefore caution is necessary in applying eq 1 for these samples. The same value may be used for the exponent of $\bar{M}_w$ in eq 1, since it does not depend upon the DP distribution of the sample, while the constant before $\bar{M}_w$ may have to be modified for the PBA samples having DP distribution other than the most probable.

*DP Distribution of the Resultant Polymer*

Since the original polymer has been prepared through the condensation polymerization, its frequency distribution of DP is given by[5]

$$f(x) = p^{x-1}(1-p) \qquad (2)$$

where $x$ is DP and $p$ denotes the probability that one functional group of $p$-aminobenzoic acid reacts. The number and weight averages of DP are thus given by

$$\bar{x}_{n(0)} = \frac{1}{1-p}, \quad \bar{x}_{w(0)} \simeq 2\bar{x}_{n(0)} \qquad (3)$$

where the subscript (0) denotes the original polymer.

One end of an original polymer molecule is assumed to react with an end of the neighboring molecule with the probability, $q$, independent of DP. Then, the probability that $m$ molecules of the original polymer, DP's of which are $x_1, x_2, \ldots, x_m$, condense into one molecule with DP of $x = x_1 + x_2 + \cdots + x_m$ will be expressed as

$$g_m(x) = \sum_{x=x_1+x_2+\cdots+x_m} q^{m-1}(1-q)f(x_1)f(x_2)\cdots f(x_m) \qquad (4)$$

The summation in this equation includes all cases where $x = x_1 + x_2 + \cdots + x_m$. Introduction of eq 2 into eq 4 leads to

$$g_m(x) = (1-p)(1-q)_{x-1}C_{m-1}p^{x-m}[(1-p)q]^{m-1} \qquad (5)$$

Consequently, the resultant frequency distribution of DP is

$$g(x) = \sum_{m=1}^{x} g_m(x)$$
$$= [p + (1-p)q]^{x-1}\{1 - [p + (1-p)q]\} \qquad (6)$$

In comparison with eq 2 it is apparent that $g(x)$ is again the most probable distribution. The number- and weight-average DP's of the resultant polymer are given by

$$\bar{x}_n = \frac{\bar{x}_{n(0)}}{1-q}, \quad \bar{x}_w \simeq \frac{\bar{x}_{w(0)}}{1-q} \qquad (7)$$

Thus eq 1 can be applied also to the resultant polymer.

The intrinsic viscosity for the original polymer, $[\eta]_{(0)}$, and for the resultant polymer, $[\eta]_{con}$, may be written as

$$[\eta]_{(0)} = K\bar{x}_{w(0)}^{\alpha} \qquad (8)$$

$$[\eta]_{con} = K\bar{x}_w^{\alpha} \qquad (9)$$

In the solution in DMAc containing 3-wt% LiCl at 20°C, $\alpha = 1.85$ and $K$ is estimated from eq 1 to be $1.10 \times 10^{-4}$ by putting the molecular weight of the monomer of PBA as 119. The exponent $\alpha$ in eq 8 and 9 depends usually upon the expansion factor of a polymer chain in solution. Since PBA is a rigid polymer, however, the solvent and temperature will not affect $\alpha$. Hence, the same value of $\alpha$ may be applicable also in conc $H_2SO_4$ at 30°C. The value of $K$ is obtained as $1.06 \times 10^{-4}$ from eq 8 by comparing $[\eta]$ measured for the sample H-1 in DMAc containing 3-wt% LiCl with that in conc $H_2SO_4$ at 30°C. From eq 7—9 is derived the relation

$$q = 1 - \left\{ \frac{[\eta]_{(0)}}{[\eta]_{con.}} \right\}^{1/\alpha} \qquad (10)$$

It may be worth noting that possible error introduced in the above calculation of $K$ does not enter into the estimation of $q$. The values of the weight average DP, $\bar{x}_w$, molecular weight, $\bar{M}_w$, and $q$ for the L- and H-series samples were calculated through use of eq 8—10 and are shown in Tables I and II.

*Various Quantities Characterizing the Reaction*

The expected value for $m$, $E(m)$, is derived from eq 5 and 6 as follows

$$E(m) = \sum_{x=1}^{\infty} \left\{ g(x) \frac{\sum_{m=1}^{x} mg_m(x)}{\sum_{m=1}^{x} g_m(x)} \right\}$$

$$= 1 + q \tag{11}$$

The seventh columns in Tables I and II indicate the values for $E(m)$.

The frequency fraction corresponding to each value of $m$ of the resultant polymer can be calculated as

$$\frac{\sum_{x=m}^{\infty} g_m(x)}{\sum_{x=1}^{\infty} g(x)} = q^{m-1}(1-q) \tag{12}$$

This fraction decreases with increasing $m$, implying that the fraction of the unreacted polymers ($m=1$) is the largest. On the other hand, the weight fraction of the species corresponding to each values of $m$ is given by

$$\frac{\sum_{x=m}^{\infty} xg_m(x)}{\sum_{x=1}^{\infty} xg(x)} = mq^{m-1}(1-q)^2 \tag{13}$$

As a function of $m$, this shows a single maximum at

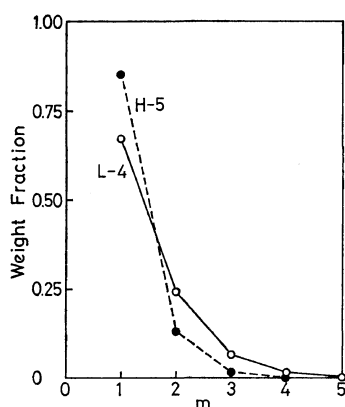$$\frac{1}{1-q} \geq m \geq \frac{q}{1-q} \tag{14}$$



**Figure 1.** The weight distribution of the polymer consisting of the original PBA plotted against the "degree of polymerization." Open and filled circles indicate the sample L-4 obtained by annealing the original PBA having low DP in the solid-crystalline state and the sample H-5 obtained by annealing the original PBA having high DP in liquid-crystalline state, respectively.

If $q$ is larger than one half, the value of $m$ satisfying eq 14 is larger than unity. In the present case, however, the weight fraction of the unreacted polymers is the largest as is evident from the $q$ values in the tables. Figure 1 shows plots of the weight fraction given by eq 13 for the L-4 and H-5 samples against $m$. This indicates that about one fourth by weight of the resultant polymers annealed in the solid-crystalline state and 13 wt% of those annealed in the liquid-crystalline state for 24 hr are the dimers of the original PBA.

The molecular weight of the original polymer is not uniform. Consequently, there are dual ways representing the conversion of the condensation reaction, one being by frequency and the other by weight. The latter will be defined by

$$\text{Conversion by weight} = 1 - \frac{\sum_{x=1}^{\infty} xg_1(x)}{\sum_{x=1}^{\infty} xg(x)}$$

$$= q(2-q) \tag{15}$$

This conversion is shown in the last columns of Tables I and II.

The values of $q$ even for the samples reacted for the longest time, L-4 and H-5, are quite low as compared with the $p$ values of 0.98 and 0.99 calculated by eq 3 for the original polymers of L-1 and H-1, respectively. This is due simply to the fact that the reaction occurred in the solid- and liquid-crystalline states. It is, however, particularly remarkable that the total conversion from the original PBA into its dimer, trimer and so on exceeds 30 wt% in the solid state (the sample L-4) and attains 15 wt% in the liquid-crystalline state (the sample H-5), respectively, at 200°C for 24 hr.

Anyway, it is evident that the condensation reaction took place between fairly large amounts of the chain ends of the original polymer. There have not been published many papers concerning such "polymerization" of polymers. The frequency of the condensation should depend on the molecular arrangements in the reaction systems. The molecular arrangements in these cases are supposed to be nematic as was mentioned previously. It can be concluded, therefore, that the reaction occurred mainly in the way of

"head to tail" of the two molecules in the nematic systems. Moreover, depending on the molecular arrangements, three or more original polymer molecules can be "polymerized" linearly along the molecular axis. It is also likely that this sort of condensation reaction takes place more frequently in the solid- and liquid-crystalline states than in the molecularly dispersed solution.

The values of $q$ and the conversion were higher for the L-series samples than those obtained for the H-series samples. This means that the reactivity of PBA in the solid-crystalline state is higher than that in the liquid-crystalline state in spite of the possible lower mobility of the PBA chain ends in the former state. The reaction does not appear to be affected by the mobility of the chain ends. The higher molecular weight of the original polymer in the latter case and the condition of the precipitation of the original polymer (including the possible existence of the trace of LiCl) seem to have affected the results. Moreover, one can not deny the possibility that the intentional exclusion of water

vapor evolved enhanced the condensation reaction in the case of the annealing in the solid state. In the above theoretical treatment, kinetic factors have not directly been taken into consideration, but they are all included in terms of $q$, which is time dependent. Since $q$ increases with the annealing time, a kinetic approach would be necessary including, for instance, its dependency upon the annealing temperature.

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