

Manganese(IV)-Initiated Graft Polymerization of Vinyl Monomers on Polyamide Fibers

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Synopsis

The feasibility of potassium permanganate to induce graft polymerization of vinyl monomers onto nylon 6 was investigated. The graft yield is greatly enhanced by increasing the monomer concentration, reaction time, and temperature. The addition of metallic ions as promoters to the grafting medium accelerates the graft polymerization. A mechanism for grafting was proposed. The activation energy of initiation E_i for methyl methacrylate was calculated and found to be 5 kcal/mole. The overall rate of graft polymerization R_p depends on the monomer concentration.

INTRODUCTION

The use of potassium permanganate to induce polymerization of vinyl monomers has been studied by a number of workers.^{1,2} However, its employment as initiator for graft copolymerization onto textile is limited.³⁻⁷ The effect of methanol and metallic salts on this system has not been thoroughly investigated.

In the present study, graft polymerization of methyl methacrylate, acrylonitrile, and acrylic acid was carried out onto nylon 6 fibers initiated by manganese(IV) in order to elucidate the general kinetics of the reaction.

EXPERIMENTAL

In this study, nylon 6, supplied by Misr Rayon Co. as 16-denier staple fiber, was used. The purification of these fibers was carried out by successive extraction with acetone, methanol, and water. As monomers, freshly distilled methyl methacrylate, acrylonitrile, and acrylic acid were used.

Graft polymerization was carried out as follows: A 25-ml portion of aqueous solution of potassium permanganate of known concentration was placed in a glass-stoppered Erlenmeyer flask. The latter was kept in a thermostat for 10 min at a specified temperature (30°C, 40°C, 50°C, and 60°C). The polyamide sample (0.5 g) was introduced in the flask, and the required amount of monomer, dissolved in 7.5 ml methanol, was immediately added, followed by 10 ml of 2*N* sulfuric acid; the total volume was then adjusted to 50 ml. The flask was stoppered and the polyamide sample was kept well immersed in the reaction medium. After the desired reaction time, the sample was removed, thoroughly washed with water, and air dried. The sample was

then subjected to repeated Soxhlet extraction and drying until constant weight was obtained. For extraction, acetone, dimethylformamide, and water were used as solvents for samples grafted with methyl methacrylate, acrylonitrile, and acrylic acid, respectively. Calculation of the percentage grafting was based on dry weight:

$$\text{grafting \%} = \frac{\text{dry weight of grafted sample} - \text{dry weight of sample}}{\text{dry weight of sample}} \times 100.$$

The formed homopolymer was estimated gravimetrically and determined as follows:

$$\text{homopolymer \%} = \frac{\text{dry weight of homopolymer}}{\text{weight of monomer}} \times 100.$$

The methyl methacrylate consumption during the grafting process was estimated iodometrically.⁸

RESULTS AND DISCUSSION

The factors affecting manganese(IV)-induced grafting were investigated. Variables studied included reaction time, temperature, permanganate and monomer concentrations, solvent, and kind of acid.

Permanganate Concentration

Figure 1 shows the effect of potassium permanganate concentration on the extent of grafting and on homopolymer formation when applying methyl

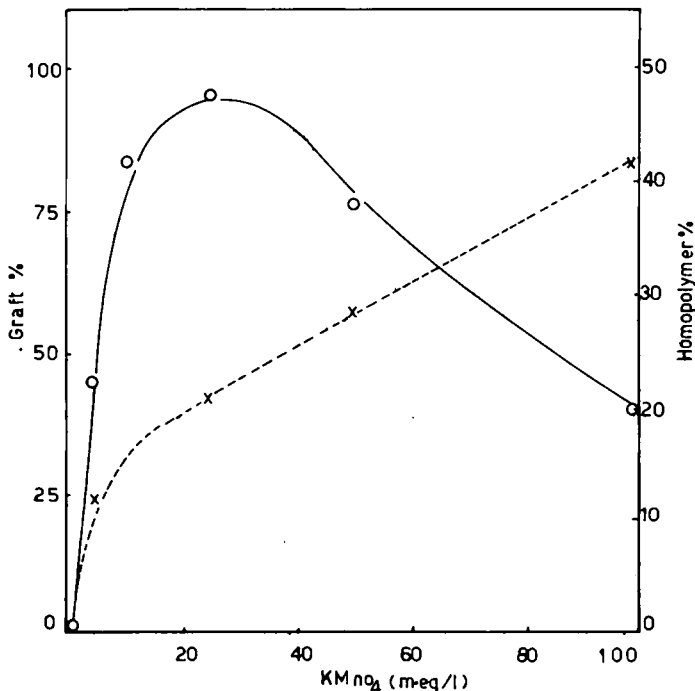
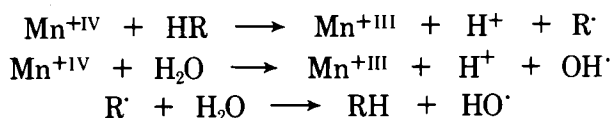


Fig. 1. Effect of potassium permanganate concentration on grafting and homopolymer formation on nylon 6: (— O) grafting %; (--- X) homopolymer %; 0.4*N* sulfuric acid, 0.552 mole/l. methyl methacrylate at 50°C, 3 hr, and a material:liquor ratio of 1:100.

methacrylate onto nylon 6. Obviously, increasing the initiator concentration up to 25 meq/l. causes a rapid increase in the graft yield. Further increase in potassium permanganate concentration causes a decrease in the extent of graft formation; this is in agreement with previous work on cellulose.⁶ On the other hand, the homopolymer formation is increased on increasing the initiator concentration. It has been reported⁴ that free-radical formation in a polymerization system initiated by potassium permanganate in the presence of an acid seems likely to occur through reduction of manganese(IV) to manganese(III) and/or manganese(II). Thus, during vinyl copolymerization on nylon under the catalytic influence of potassium permanganate in the presence of an acid (HR), creation of free radicals in the system may be represented as follows:



The graft yield would be greatly enhanced if the free radicals formed on nylon are capable of capturing the monomer.

The formation of the homopolymer certainly competes with grafting, since it lowers the initiator as well as the monomer concentration in the reaction medium. The data show that the graft yield increases with increasing the initiator concentration and attains a maximum at 25 meq KMnO_4 /l. Further

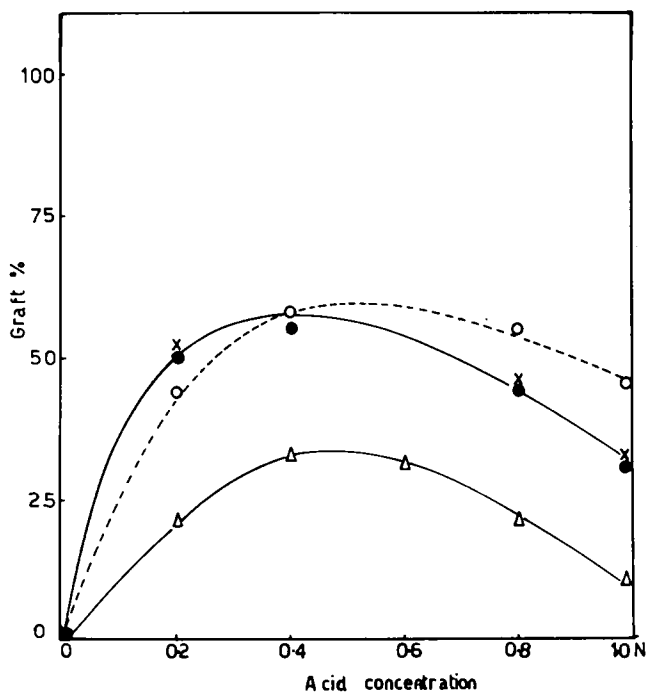


Fig. 2. Effect of acid concentration on grafting: (— O) sulfuric acid; (— ●) nitric acid; (— X) perchloric acid; (— A) oxalic acid; 25 meq/l. KMnO_4 , 0.552 mole/l. methyl methacrylate at 50°C, 3 hr, and a material:liquor ratio of 1:100.

increase in the permanganate concentration results in a decrease in the graft yield. On the other hand, the homopolymer increases gradually with increase in permanganate concentration. The decrease in the graft yield may be explained by termination of most of the formed reactive sites by the exceedingly formed free radicals in presence of high concentrations of permanganate.

Effect of Acids

It is evident that the presence of an acid in the graft copolymerization system initiated by potassium permanganate is essential. It is therefore of interest to study the effect of both kind and concentration of the acid on graft yield. Figure 2 shows this effect when using perchloric, nitric, sulfuric, and oxalic acids.

Regardless of the kind of acid employed, the graft yield increases with increasing acid concentration and attains a maximum, but falls again at higher concentrations. The relatively low graft yield at higher acid concentration has been discussed and attributed to a variety of reasons.¹ Our data indicate that the effectiveness of the acids follow the order: sulfuric acid > nitric or perchloric acid > oxalic acid. This may be attributed partly to some side reactions such as formation of molecular oxygen, being pronounced in case of perchloric or nitric acid. It may be attributed also to the affinity and/or the half-life time of the different acid radicals which seem to follow the same order as their efficiency in inducing grafting.

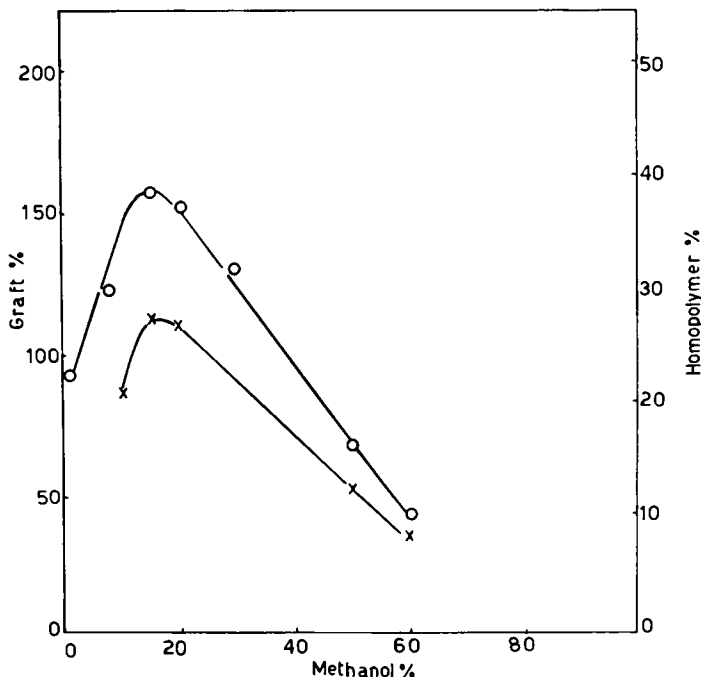


Fig. 3. Effect of methanol concentration on grafting and homopolymer percentages: (— O) grafting %; (— X) homopolymer %; 25 meq/l. KMnO_4 , 0.552 mole/l. methyl methacrylate, 0.4N sulfuric acid, 50°C, 3 hr, and a material:liquor ratio of 1:100.

Effect of Methanol Concentration

In the light of previous studies^{9,10} dealing with the effect of solvents in graft polymerization, we have chosen methanol as solvent for grafting. Results of this study are shown in Figure 3.

It is evident from the data that a significant enhancement in both graft and homopolymer yields is achieved on using methanol as solvent in the polymerization medium. This increase reaches a maximum at a methanol concentration of 15% (Fig. 3). However, on using higher amounts of methanol, a marked decrease in both the graft yield and homopolymer formation takes place. This decrease may be attributed to exhaustion of most of the formed free radicals in oxidation of methanol¹¹ and/or to termination of the growing polymer chains, grafted onto the substrate, via chain transfer giving rise to free methanol radicals. The same phenomenon was observed by other investigators.^{9,10}

Effect of Temperature

Figure 4 shows that increasing the temperature from 30° to 60°C enhances the rate of grafting considerably. Similar trends have been reported in grafting wool and cellulose using the same initiator.^{5,6} In the present work, we tried to find out the activation energies of the reaction. For this purpose, we used Arrhenius equation by plotting $\log R_p$ versus $1/T$ (Fig. 5), and the activation energy was found to be 7.5 kcal/mole.

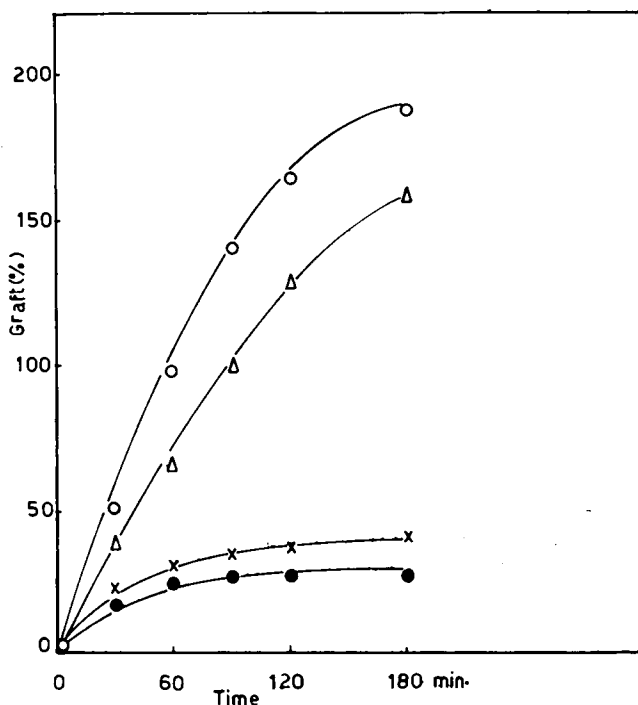


Fig. 4. Effect of temperature on grafting percentage: (— O) 60°C; (— A) 50°C; (— X) 40°C; (— ●) 30°C; 25 meq/l. KMnO_4 , 0.552 mole/l. methyl methacrylate, 15% methanol, 0.4N sulfuric acid, 3 hr, and a material:liquor ratio of 1:100.

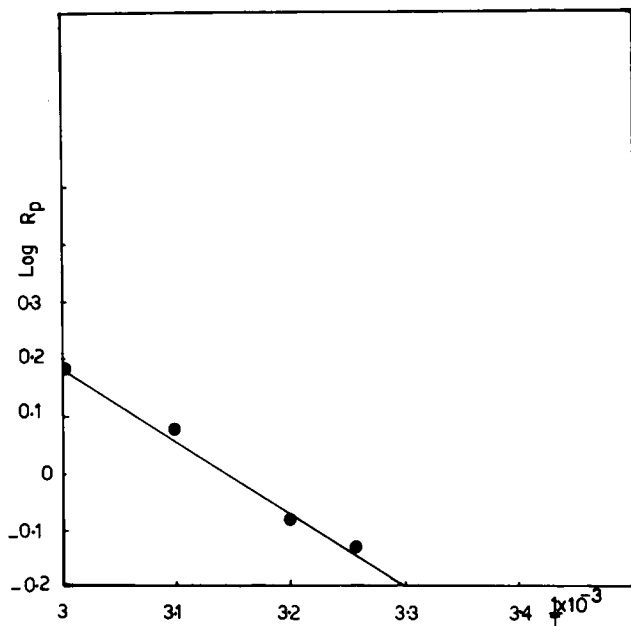


Fig. 5. Logarithms of initial rate of graft polymerization R_p of methyl methacrylate vs. $1/T$, 25 meq/l. KMnO_4 , 15% methanol, 0.4N sulfuric acid, 0.552 mole/l. methyl methacrylate at 50°C , 3 hr, and a material:liquor ratio of 1:100.

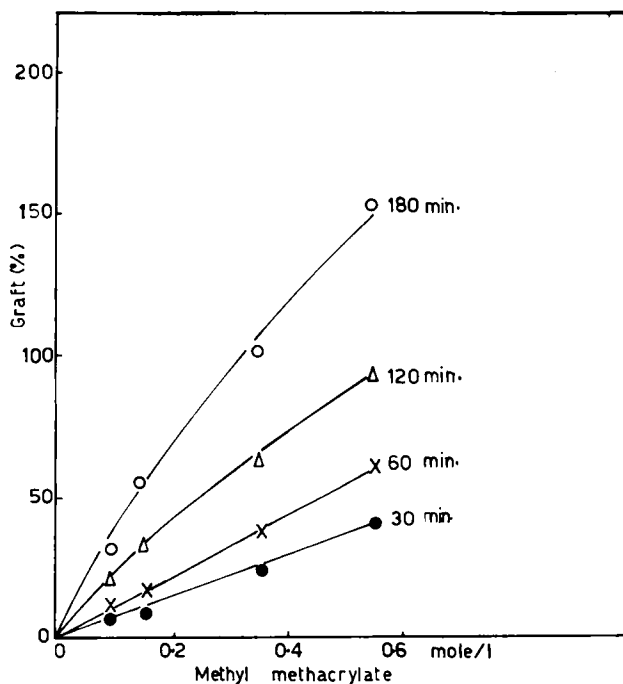


Fig. 6. Effect of methyl methacrylate concentration on grafting percentage: (—○) 0.552 mole/l.; (—△) 0.368 mole/l.; (—X) 0.184 mole/l.; (—●) 0.092 mole/l.; 25 meq/l. KMnO_4 , 15% methanol, 0.4N sulfuric acid, 50°C , and a material:liquor ratio of 1:100.

The apparent overall activation energy E_a can be represented by the following equation:

$$E_a = E_p + \frac{1}{2}(E_i - E_t)$$

where E_i , E_p , and E_t are the activation energies of initiation, propagation, and termination, respectively.

Previous investigators¹² have reported that the value $E_p - (E_t/2)$ is equal to 5 kcal/mole for methyl methacrylate. On using this value and substituting in the above equation, it is found that E_i is equal to 5 kcal/mole, which is much lower than E_i in other redox systems.^{13,14}

Effect of Monomer Concentration

Figure 6 illustrates the effect of methyl methacrylate concentration on the extent of grafting. It is clear that the graft yield is higher the higher the amount of methyl methacrylate in the system, and the same holds true for the total conversion. This agrees with previous studies^{5,15} which ascribed this to gel effect brought about as a result of the solubility of poly(methyl methacrylate) in its own monomer. Moreover, complex formation between nylon 6 and methyl methacrylate^{16,17} is more favorable at higher methyl methacrylate concentration.

The graft yield varies according to the monomer used and has the order: methyl methacrylate > acrylonitrile > acrylic acid (Fig. 7), which may indi-

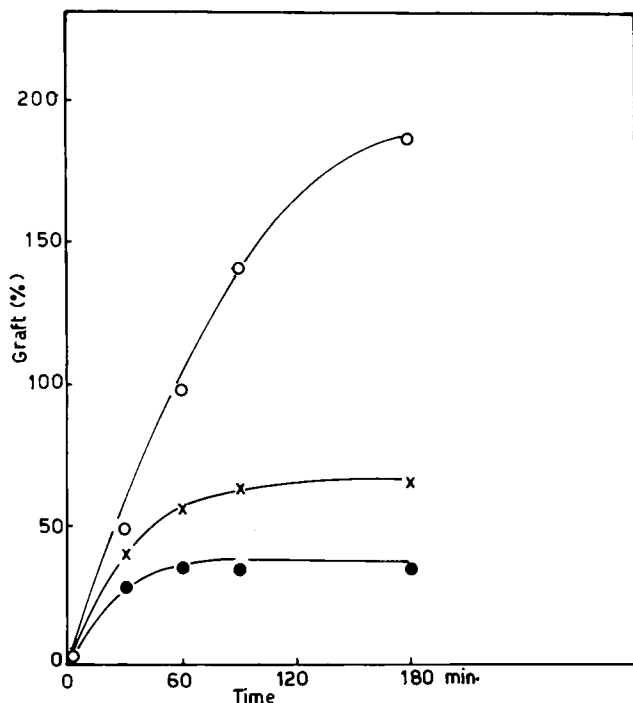


Fig. 7. Graft yield of different monomers: (— O) 0.552 mole/l. methyl methacrylate; (— X) 0.932 mole/l. acrylonitrile; (— ●) 0.833 mole/l. acrylic acid; 25 meq/l. KMnO_4 , 15% methanol, 0.4*N* sulfuric acid, 3 hr, 60°C, and a material:liquor ratio of 1:100.

TABLE I
 Graft Polymerization (percent) of Methyl Methacrylate
 Onto Nylon-6 in Presence of Various Metallic Ions
 (0.4*N* Sulphuric acid, 6% Methyl Methacrylate, 15% Methanol, 3 hours, 60 C°)

| Metallic ion concentration, m.mole/l | Graft Polymerization, % | | |
|--------------------------------------|-------------------------|------------------|-----------------|
| | Fe ³⁺ | Cu ²⁺ | Li ⁺ |
| Nil | 156 | 156 | 156 |
| 2.5 | 310 | 304 | 290 |
| 5.0 | 310 | 310 | 304 |
| 7.5 | 314 | 309 | 316 |
| 10.0 | 314 | 310 | 328 |

cate higher reactivity of methyl methacrylate for both polymerization and grafting in the presence of polyamide.^{18,19}

Effect of Metallic Ions

The effect of various promoting metallic ions on the graft polymerization of methyl methacrylate onto nylon 6 was investigated. Nylon 6 samples were immersed and left overnight in various concentrations (2.5–10 mmole/l.) of lithium chloride, copper sulfate, and ferric sulfate. The different ingredients of grafting were then added as mentioned in the experimental part. The results of this investigation are shown in Table I.

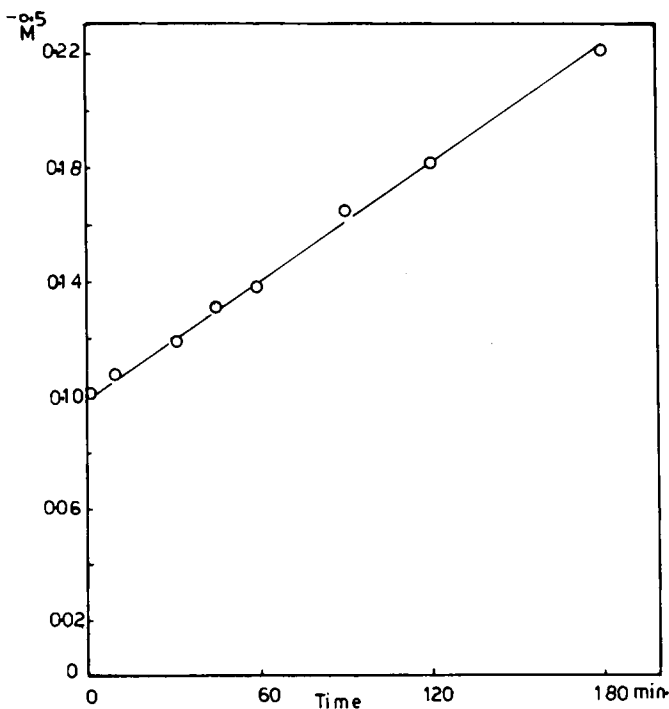


Fig. 8. Instantaneous methyl methacrylate concentration $[M]^{-0.5}$ plotted as a function of time in minutes, 25 meq/l. $KMnO_4$, 15% methanol, 0.4*N* sulfuric acid, 0.552 mole/l. methyl methacrylate, 3 hr, and a material:liquor ratio of 1:100.

The data indicate that the addition of these metallic ions greatly enhances the graft polymerization and is independent of the concentration, the type, and/or the valence of the cation used.

The great enhancement in the graft yield may be attributed to formation of a complex between the polar groups of the monomer and the metal ions resulting in delocalization of the electrons in the double bond of the complexed monomer.²⁰⁻²²

Gaylord has explained such phenomena on the basis of formation of a complex between the added cations and the monomer giving rise to a donor-acceptor complex in which the uncomplexed monomer behaves as a donor relative to the complexed one.²³ It is worth mentioning that Bamford et al.²⁴ have reported that addition of lithium chloride increased the propagation coefficient without affecting the termination factor.

Course of Reaction

The methyl methacrylate consumption during the course of conversion of monomer to grafted polymer on polyamide was investigated through the estimation of unsaturation using an iodometric method.⁸

In order to detect the reaction order, the instantaneous monomer concentration $[M]$ at time t was plotted as a function of time in several ways: $[M]^{-1/2}$, $[M]^{-1}$, or $[M]^{-3/2}$. A straight relationship was found to exist only between t and $[M]^{-1/2}$. This is illustrated in Figure 8. In other words,

$$[M]^{-1/2} = K_1 t + C$$

where K_1 is the slope and C is the intercept of the straight line. By differentiation,

$$\frac{-d[M]}{dt} = R_p = 2K_1[M]^{3/2}$$

where R_p is the overall rate of the graft polymerization of methyl methacrylate on nylon. This indicates that the overall rate of polymerization depends on the monomer concentration. It must be mentioned that the monomer consumption includes also homopolymer formation, but the extent of this formation can be neglected.

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