

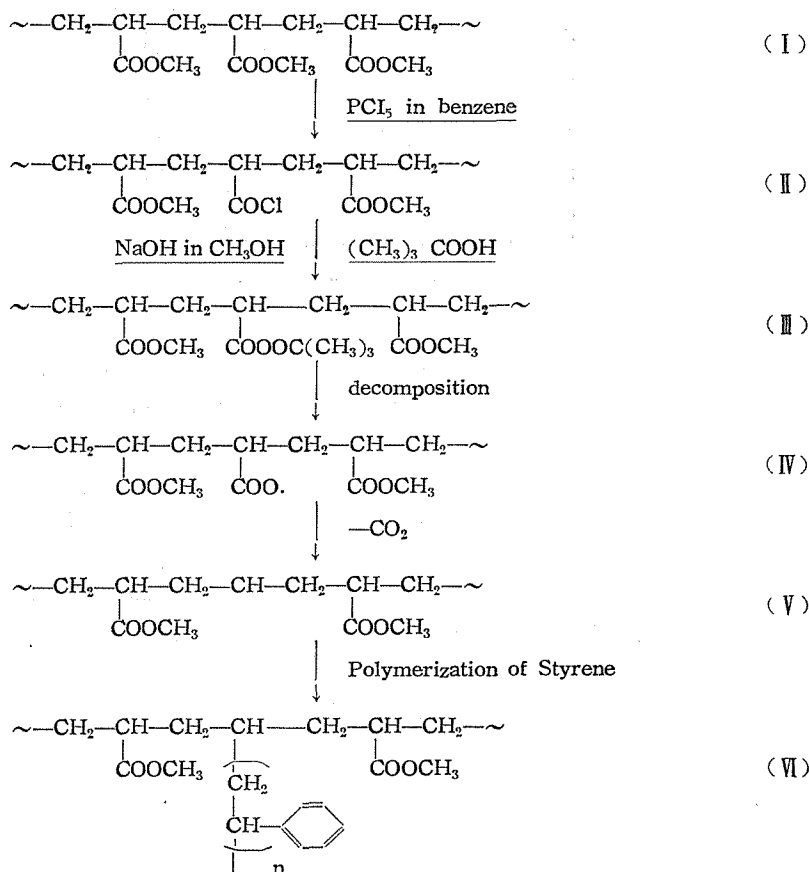
## 5. Vinyl-Polymerization Initiated by Polyradical. (I)

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The formation of the so-called "graft-copolymer" has been studied by several groups of workers in recent years, and it was based on the chain-transfer mechanism between radical and polymer.

The present investigation was undertaken to synthesize the polymer which produces polyradical by thermal decomposition and to prepare graft-copolymer which consists of the backbone of the polymer catalyser and the branches of another vinyl monomer. The partial perester of polymethylacrylate (PMA) was synthesized and was used as an initiator of the polymerization of styrene. The synthetic method of perester is as follows :



PMA (I) and  $\text{PCl}_5$  (molar ratio ranging from 1 : 1 to 1 : 2) were dissolved in benzene and refluxed for 9.5–12 hrs. The acid chloride unit was introduced in PMA, the content of acid chloride unit being controlled to be ranged from 22 to 38% of the total carbomethoxyl groups by varying the molar ratio of PMA and the reaction time. Then, (II) was dissolved in *t*-butylhydroperoxide and NaOH in  $\text{CH}_3\text{OH}$  (equivalent to  $-\text{COCl}$ ) was added dropwise to the solution under vigorous agitation at room temperature. A part of acid-chloride unit was changed to perester unit and the other part to methyl ester unit. The partial perester of polymethylacrylate (III), containing 4.9% and 6.0% of perester unit, was obtained from the partial chloride (II) containing 25.6% and 37.8% of acidchloride unit, respectively. The analysis of active oxygen was made according to K. Nozaki (*Ind. Eng. Chem. Anal. Ed.* 18, 583 (1946)).

Styrene was polymerized by the polymer perester (III) at  $70^\circ \pm 0.5^\circ\text{C}$  for 4 hrs. in sealed tubes. The results are given in the following table.

Table 1.

| Tube no.   | Catalyst         |                                  | Polymerization % |
|------------|------------------|----------------------------------|------------------|
|            | Source           | Active oxygen mole $\times 10^4$ |                  |
| 1 }<br>2 } | polymer perester | 2.58                             | 7.3              |
|            |                  | 12.62                            | 14.9             |
| 3          | BTO              | 4.14                             | 17.9             |
| 4          | no catalyst      | 0                                | 0                |

(The common composition : styrene 10 c.c. methanol 2.5 c.c.)

The graft copolymer thus obtained (tube no. 2) was slightly soluble in benzene and viscosities at various concentrations were measured in benzene at  $30^\circ$  (Fig. 1).

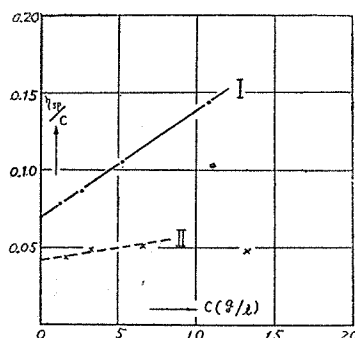


Fig. 1. Viscosities of graft and linear polymers at  $30^\circ\text{C}$ .

I: Graft polystyrene (in tube 2)

II: Linear polystyrene (in tube 3)

The graft copolymer was hydrolyzed by refluxing with aqueous alkali for 20 hrs. and

the polymer thus treated was insoluble neither in benzene and other organic solvents nor in aqueous alkali.

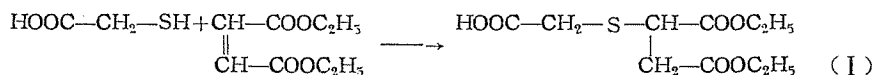
## 6. Free Radical Reactions

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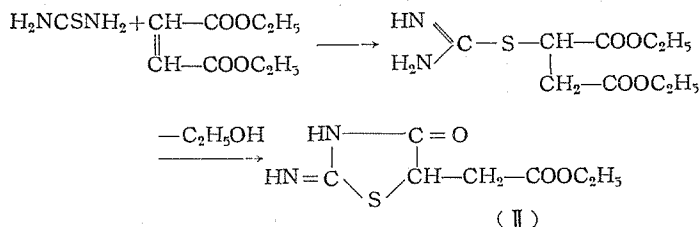
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### 1. Reactions of mercaptoacetic acid and thiourea with diethyl maleate.

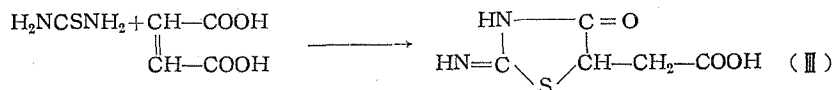
Mercaptoacetic acid did not react with diethyl maleate without catalyst, while in the presence of small amount of ammonium hydroxide or benzoyl peroxide diethyl carboxymethylmercaptosuccinate (I) (b.p. 194–200°/5mm.) was obtained. The yields of (I) were 78.4% and 92.7% of calcd. value respectively. The reaction mechanism seems to be analogous to that of the reaction between mercaptoacetic acid and methyl acrylate (M. S. Kharasch, *J. Org. Chem.*, **13**, 97 (1948)).



Thiourea  $\text{H}_2\text{N}-\text{C}(=\text{S})-\text{NH}_2$  reacts in the form of  $\text{HN}=\text{C}(\text{SH})-\text{NH}_2$  in many cases and is regarded as a sort of mercaptan. It is expected, therefore, that thiourea adds to diethyl maleate in the same way as mercaptoacetic acid does. Thiourea reacted with diethyl maleate in alcohol, and ethyl pseudothiohydantoin acetate (II) (m. p. 164–6°) was found as the product. The effect of benzoyl peroxide as a catalyst was not profound and it increased the yield of (II) a little.



Thiourea and maleic acid gave the addition compound (m. p. >238°) which was considered to be a salt or condensate of some molecules of pseudothiohydantoinacetic acid (III). Any accelerating effect of benzoyl peroxide was not observed in this reaction.



Probably (II) and (III) are obtained, not by a radical addition, by an ionic addi-