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Kinetic Studies of the Solution Polymerization of Trioxane Catalyzed by $BF_3 \cdot O(C_2H_5)_2$. III. The Effect of the Monomer Concentration

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In the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$, the dependence of the monomer concentration on the polymerization reaction has been studied. The kinetic order of the monomer concentration as determined from the course of polymerization is close to 2 (except in a non-polar solvent). The kinetic order of the initial monomer concentration is extraordinarily large in the polar solvent. On the other hand, the molecular weight of the polymers formed increases with an increase in the initial monomer concentration. In the polymerization of trioxane in a polar solvent such as nitrobenzene at a low monomer concentration, the molecular weight of the polymers does not increase in the course of polymerization, even at the initial stage of polymerization. The reason for this has been discussed in terms of the nature of the chain carrier.

It has been recognized that, in the cationic, solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$, the molecular weitht of the resultant polymers increases in the course of polymerization, not as in the cationic polymerization of vinyl monomers.¹⁾ This has been explained in terms of the rate of the propagation reaction being smaller than that of the initiation reaction. It has been suggested as the cause of this that the chain carrier in the solution polymerization of trioxane is not a carbonium ion but a stable oxonium ion solvated by monomers. If a condition were selected so that a more reactive carbonium ion than the oxonium ion were easily produced or the reactivity of initiating species were decreased, it might be expected that the relation between the conversion and the molecular weight of polymers would be changed.

Since a decrease in the trioxane concentration corresponds to a decrease in the concentration of the monomeric ether group which solvates the active ends, the behavior of the cationic polymerization of trioxane at a low monomer concentration will be studied in this paper.

It should also be noted that the effect of the catalyst and water concentrations on the polymerization rate is complicated and that the kinetic order of these concentrations varies remarkably with the kind of solvent.²⁾ Because of this, as well as for the above-mentioned purpose, the effect of the monomer concentration on the polymerization rate has been studied.

As a result, we have found that the kinetic order of the initial monomer concentration to the initial rate is large and that the molecular weight of the polymers produced at a low monomer concentration in a solvent with a high dielectric constant is nearly constant at the initial state of polymerization.

Experimental

The procedures of the polymerization and purification of materials were the same as were used in the first paper.²⁾ The molecular weights of the polymers formed were compared by the viscosity numbers (η_{sp}/C), which were measured in a *p*-chlorophenol solution.¹⁾

Results

The Effect of the Monomer Concentration on the Rate of Polymerization.—As non-polar solvents, such as *n*-hexane, do not have a high solubility toward trioxane, ethylene dichloride was used as a polar solvent and nitrobenzene, as a highly-polar solvent.

The time-conversion curves at various monomer concentrations in ethylene dichloride at a fixed catalyst concentration are shown in Fig. 1. With an increase in the initial monomer concentration, the rate of polymerization increased and the induction period decreased. Figure 2 shows the logarithmic plot of the initial monomer concentration against that of the initial rate as determined graphically from Fig. 1. It may be seen that the kinetic order of the initial monomer concentration to the initial rate is approximately 3.

In Fig. 3 is similarly shown the time-conversion curves at various monomer concentrations in nitrobenzene. It may be seen that the effect of the initial monomer concentration on the initial rate was remarkably large. In fact, on plotting the initial rate against the initial monomer concen-

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1) T. Higashimura, T. Miki and S. Okamura, This Bulletin, **39**, 25 (1966).

2) T. Higashimura, T. Miki and S. Okamura, ibid., **38**, 2067 (1965).

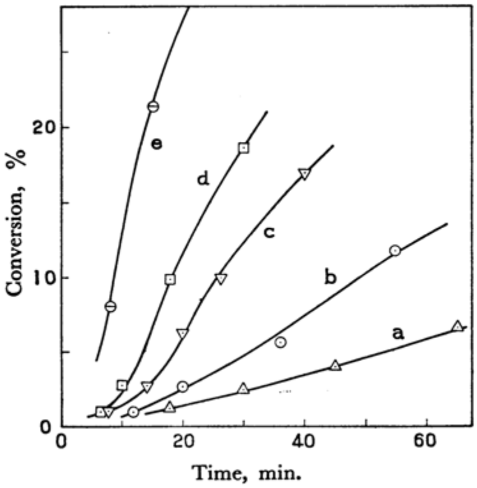

Fig. 1. Effect of the monomer concentration on the rate of polymerization in ethylene dichloride at 30°C.
$[BF_3 \cdot O(C_2H_5)_2]$; 20 mmol./l., $[H_2O]$; 2.7—3.0 mmol./l., $[M]_0$; a(△): 1.4, b(○): 1.7, c(▽): 2.2, d(□): 2.8 and e(⊖): 3.3 mol./l.

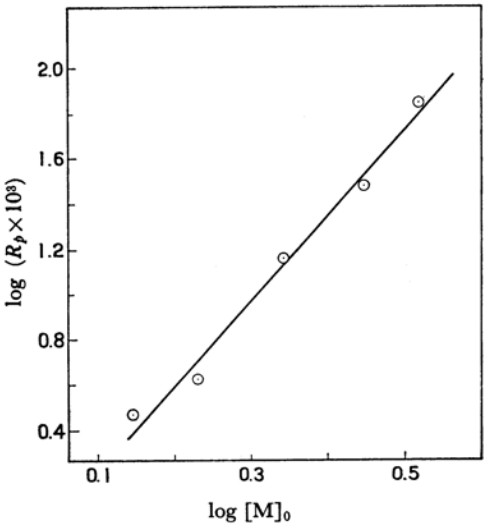

Fig. 2. Relationship between the initial rate and the initial concentration of monomer in ethylene dichloride at 30°C.
Calculated from Fig. 1.

tration, Fig. 4 was obtained; it was found that the initial polymerization rate was proportional to the sixth power of the initial monomer concentration. The induction period also decreased with an increase in the initial monomer concentration, but no simple stoichiometric relation has been found.

The Effect of the Monomer Concentration on the Molecular Weight of Polymers.—Figure 5 shows the relation between the conversion and the molecular weight of polymers obtained in ethylene dichloride at various initial monomer concentrations. The molecular weight of the

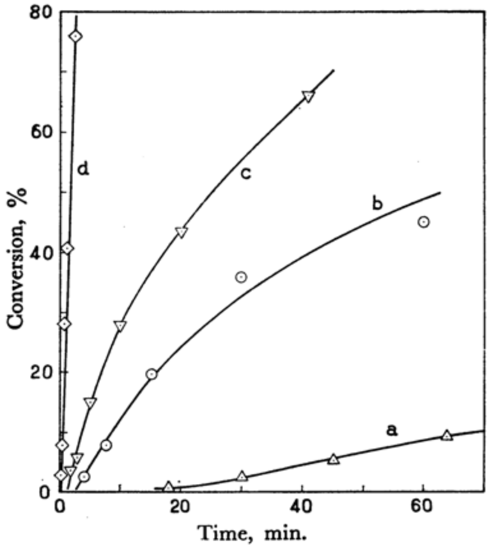

Fig. 3. Effect of the monomer concentration on the rate of polymerization in nitrobenzene at 30°C.
$[BF_3 \cdot O(C_2H_5)_2]$; 10 mmol./l., $[H_2O]$; 2.3—3.9 mmol./l., $[M]_0$; a(△): 0.83, b(○): 1.0, c(▽): 1.1 and d(◇): 2.2 mol./l.

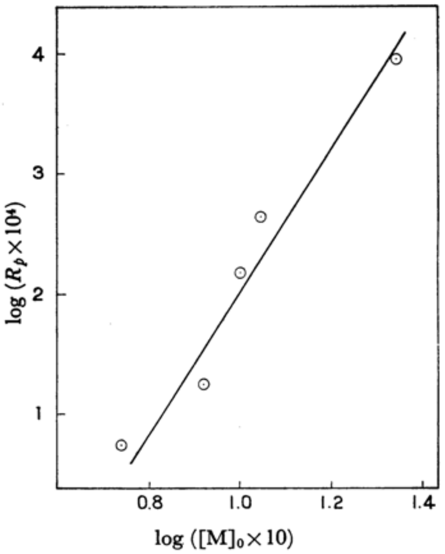

Fig. 4. Relationship between the initial rate and the initial concentration of monomer in nitrobenzene at 30°C.
Calculated from Fig. 3.

polymers increased in the course of the polymerization, even with a low initial concentration of monomer. The relation between the initial monomer concentration and the value of η_{sp}/C at the fixed conversion as determined graphically from Fig. 5 is shown in Fig. 6. The value of η_{sp}/C was proportional to the initial monomer concentration up to a 10% conversion.

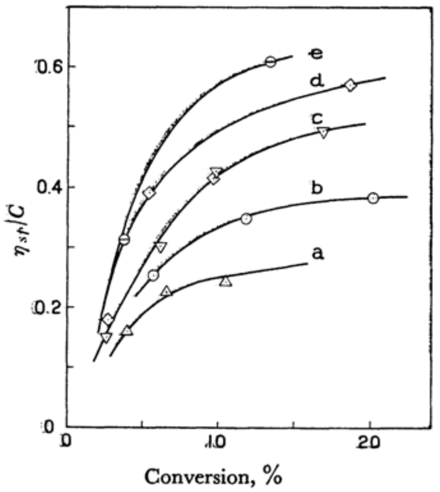

Fig. 5. Effect of the monomer concentration on the molecular weight of resultant polymers in ethylene dichloride at 30°C.
Polymerization conditions are the same as in Fig. 1. $[M]_0$; a(△): 1.4, b(○): 1.7, c(▽): 2.2, d(□): 2.8 and e(⊖): 3.3 mol./l.

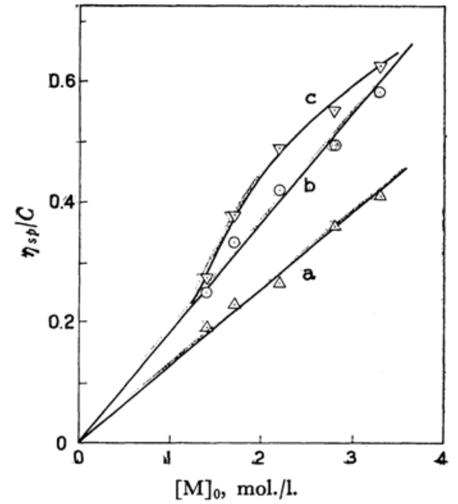

Fig. 6. Relationship between the molecular weight of polymers and the initial concentration of monomer at various conversion in ethylene dichloride at 30°C.
Calculated from Fig. 5. Conversion; a(△): 5.0, b(○): 10 and c(▽): 15%

The behavior in nitrobenzene was different. As is shown in Fig. 7, at a low initial concentration of the monomer no increase of the molecular weight with the conversion was seen in the initial state of polymerization. To clarify this unusual behavior at a low monomer concentration, a relation was obtained between the conversion and the molecular weight of polymers formed at various concentrations of catalyst and water when the initial concentration of the monomer was equal to 1.1 mol./l. The rate of polymerization with respect to this system has already been reported in a previous paper,²⁾ Figures 8 and 9 show the effects of the concentrations of the catalyst and of water respectively. In both cases the molecular weight was nearly constant, independent of the conversion, up to 30%. Figure 10 was

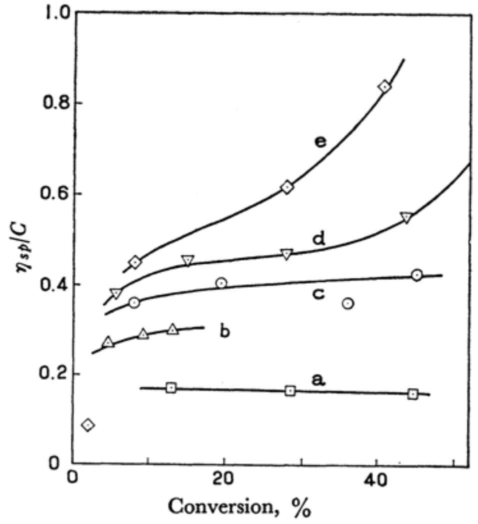

Fig. 7. Effect of the monomer concentration on the molecular weight of resultant polymers in nitrobenzene at 30°C.
Polymerization conditions are the same as in Fig. 3. $[M]_0$; a(□): 0.55, b(△): 0.83, c(○): 1.0, d(▽): 1.1 and e(◇): 2.2 mol./l.

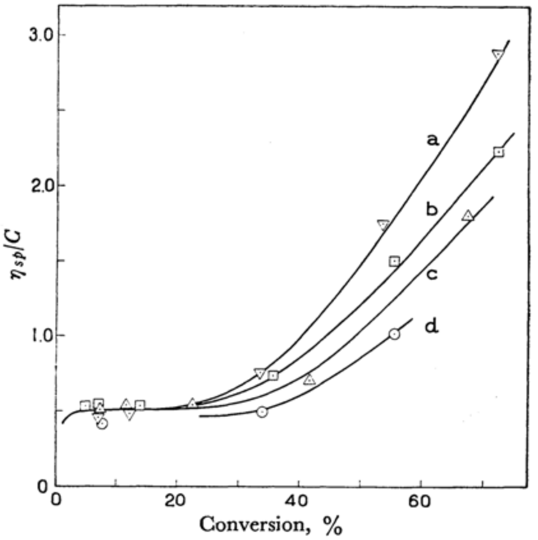

Fig. 8. Effect of the catalyst concentration on the molecular weight of resultant polymers at low monomer concentration in nitrobenzene at 30°C.
$[M]_0$; 1.1 mol./l., $[H_2O]$; 2.4 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; a(▽): 2.5, b(□): 5.0, c(△): 10 and d(○): 20 mmol./l.

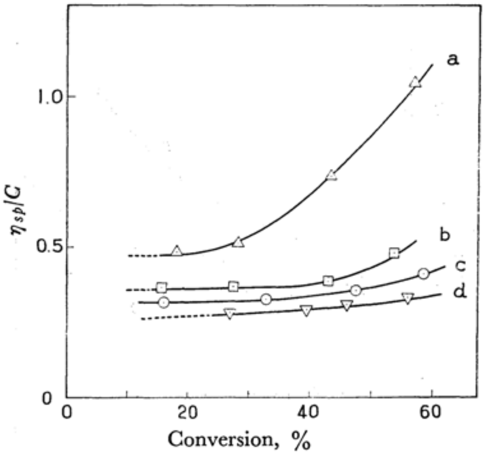

Fig. 9. Effect of the water concentration on the molecular weight of resultant polymers at low monomer concentration in nitrobenzene at 30°C. $[M]_0$; 1.1 mol./l., $[BF_3\cdot O(C_2H_5)_2]$; 10 mmol./l., $[H_2O]$; a(△): 2.2, b(□): 4.0, c(○): 5.9 and d(▽): 7.8 mmol./l.

obtained upon plotting the initial monomer concentration against η_{sp}/C at a 10% conversion as determined graphically from Fig. 7. It may be suggested that the polymerization behavior at a monomer concentration below about 1 mol./l. differs from that at a monomer concentration larger than 1 mol./l.

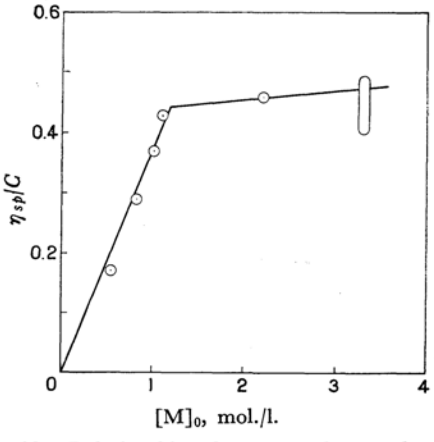

Fig. 10. Relationship between the molecular weight of polymers and the initial concentration of monomer at 10% conversion. Calculated from Fig. 7.

The Kinetic Order of Monomer Concentration as Determined from the Course of Polymerization.—The kinetic order of the monomer concentration to the polymerization rate can be determined from the relation between the polymerization rate and the residual monomer concentration at a settled time in the time-conversion curve.

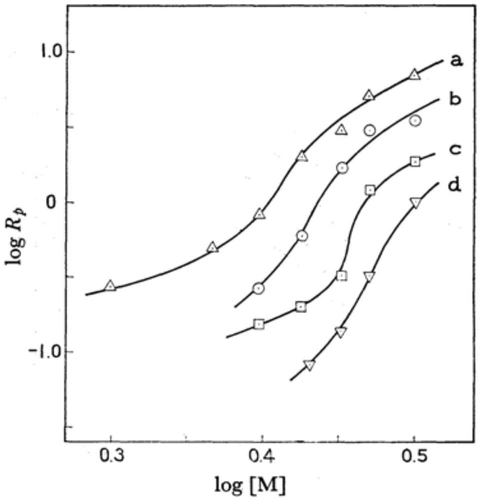

Fig. 11. Relationship between the rate of polymerization and the residual monomer concentration in the course of polymerization in ethylene dichloride at various temperatures. $[M]_0$; 3.3 mol./l., $[BF_3\cdot O(C_2H_5)_2]$; 5.0 mmol./l., Polymerization temp.; a(△): 46, b(○): 38.5, c(□): 30 and d(▽): 23°C

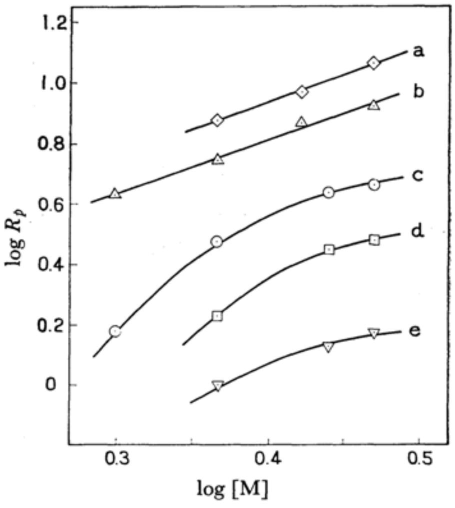

Fig. 12. Relationship between the rate of polymerization and the residual monomer concentration in the course of polymerization in nitroethane at various temperatures. $[M]_0$; 3.3 mol./l., $[BF_3\cdot O(C_2H_5)_2]$; 2.5 mmol./l., $[H_2O]$; 2.7 mmol./l., Polymerization temp.; a(◇): 50, b(△): 45, c(○): 38, d(□): 30 and e(▽): 23°C

The results of the analysis of the time-conversion curves of polymerization carried out in the various solvents are shown in Figs. 11, 12 and 13, where the concentrations of the monomer and of the catalyst were fixed and where only the reaction temperature was varied. (All the time-conversion curves will be shown in the fifth paper of this series.)

Excluding the complicated behavior in ethylene dichloride and that at a very low temperature, it may be concluded that the kinetic order of monomer concentration as determined from the course of polymerization is close to 2.

Although an abnormality was found in the relation between the conversion and the molecular weight in nitrobenzene at a low initial monomer concentration, the kinetic order of monomer concentration as determined from the course of polymerization was close to 2 in these systems, much as in systems with a high monomer concentration.

Discussion

The relation between the initial monomer concentration and the polymerization rate is very complicated, as is the relation between the catalyst or water concentration and the polymerization rate. Particularly, it was found that the initial polymerization rate is proportional to the sixth power of the initial monomer concentration in nitrobenzene

On the other hand, the kinetic order of the monomer as determined from the course of the time-conversion curve was close to 2 over a wide range of conversion in a polar solvent such as nitrobenzene, as is shown in Fig. 13. The constant kinetic order of the monomer over the wide range of conversion suggests that, in spite of the heterogeneous polymerization, a kinetic treatment is possible just as in an homogeneous polymerization. In the polymerization at a low temperature and in a less-polar solvent, however, the polymerization rate decreased remarkably in the course of the polymerization reaction. This may be due to the fact that the concentration of the active center was decreased remarkably by the precipitation of the resultant polymers, including catalysts. In a less-polar solvent it may be also considered that the rapid decrease in the polymerization rate in the course of the polymerization reaction is caused by the consumption of water as a co-catalyst.

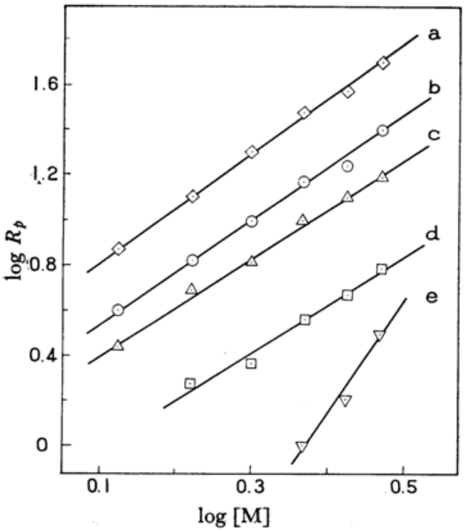

Fig. 13. Relationship between the rate of polymerization and the residual monomer concentration in the course of polymerization in nitrobenzene at various temperatures.
$[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 2.5 mmol./l., $[H_2O]$; 3.6 mmol./l., Polymerization temp.; a(◇): 30, b(△): 23, c(○): 15, d(□): 8.0 and e(▽): 3.0°C

While the kinetic order of the monomer as determined from the course of polymerization was close to 2, the kinetic order of the initial monomer concentration was extraordinarily large in the polar solvent. This suggests that the monomer or solvents participate in processes other than the propagation reaction. In a previous paper,(1) the relation between the polymerization conditions and the molecular weight of the polymers formed was explained on the assumption of the simple elementary reactions. The expression for the rate of polymerization derived from such simple elementary reactions, however, can not explain the kinetic order of the monomer. An explanation of this will be given in the next paper.(4)

Another remarkable result of the change in the monomer concentration was that, at a low monomer concentration, the molecular weight of the polymers formed was constant, independent of the conversion up to a 20—40% conversion in nitrobenzene.

In a previous paper(1) the increase in the molecular weight of the polymers formed with the conversion at the initial stage of polymerization was considered to be due mainly to the rate of the initiation reaction being larger than that of the propagation and other reactions(5) It has been supposed that, for this reason, in the cationic polymerization of trioxane the chain carrier is not a carbonium ion, but a oxonium ion which is stabilized by the solvation of the former with monomers. The formation of the oxonium ion in the polymerization of cyclic ethers is due to the instability of the corresponding carbonium ion and to the high concentration of ether groups in the reaction system.(3) Therefore, if the carbonium ion is stabilized and if the concentration of ether groups is small, it may be expected that a carbonium ion with a large reactivity exists and that the rate of the propagation reaction will increase. That is, in a solvent with great solvation ability, such as nitrobenzene, the carbonium ion is stabilized and, as the monomer concentration is small (i. e., if

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3) E. g., A. M. Eastham, "The Chemistry of Cationic Polymerization," Ed. by P. H. Plesch, Pergamon Press, London (1963), p. 401.

4) T. Miki, T. Higashimura and S. Okamura, This Bulletin, **39**, 41 (1966).

5) T. Kagiya, M. Hatta and K. Fukui, *Chem. High Polymers Japan* (*Kobunshi Kagaku*), **20**, 737 (1963).

the concentration of the ether groups which solvate the carbonium ion is small), the active end will be able to exist in the form of the carbonium ion. Therefore, in the polymerization of trioxane in nitrobenzene at a low monomer concentration, the molecular weight of the polymers will not vary with the conversion as in the polymerization of vinyl monomers. The increase in the molecular weight in the course of polymerization at a high conversion may be due to the consumption of a chainbreaking or transfer reagent during the polymerization.

Of course, there is another possible explanation of this phenomenon. If the rate of the initiation reaction is decreased in the polymerization at a low monomer concentration in nitrobenzene, we will observe the more usual relationship, in which the molecular weight of the polymer is independent of the conversion.[5] This possibility will be discussed in the next paper.[4]

On the other hand, the cationic polymerization of 3, 3-bis(chloromethyl)oxethane (BCMO) is a typical example of how the reaction proceeds through the oxonium ion. In the polymerization of BCMO the molecular weight of the polymers formed was independent of the conversion.[6,7] From this point of view, it may be unreasonable to conclude that the chain carrier in the polymerization of trioxane in nitrobenzene at a low monomer concentration is not an oxonium ion. However, it could also be concluded that the rate of the initiation reaction is not so large as that of the propagation reaction. To clarify the nature of the chain carrier, a further investigation must be carried out.

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6) J. B. Rose, *J. Chem. Soc.*, **1956**, 542.
7) I. Penczek and S. Penczec, *Makromol. Chem.*, **67**, 203 (1963).