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POLYMER-SUPPORTED LEWIS ACID CATALYSTS. II. CATIONIC POLYMERIZATION OF α-METHYLSTYRENE WITH POLYSTYRENE-GALLIUM TRICHLORIDE COMPLEX AS INITIATOR

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ABSTRACT

The polymerization of α-methylstyrene catalyzed by a polymer-supported Lewis acid catalyst, polystyrene-gallium trichloride complex, is described. The kinetic equation of the cationic polymerization is $R_p = k \cdot C_{ms} \cdot C_{cat}$, and the apparent activation energy is 20.9 kJ/mol. The effect of different solvents on the polymerization rate is quite pronounced; for example, the polymerization rate decreased in the following order in the three solvents: $CH_2ClCH_2Cl < CH_2Cl_2 < CCl_4$. High molecular weight poly(α-methylstyrene) (T_g = 185°C) could be obtained at room temperature. The mechanism of the polymerization is also discussed.

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INTRODUCTION

Polymeric catalysts have been given increased attention in recent years as an important field of functional polymers. Many polymer-supported transition metal complexes have been reported as catalysts for organic reactions [1-3]. We have also reported on a number of polymer-supported Lewis-acid complex catalysts used in organic reactions with good yield [4-7]. However, very few reports on their application to polymerization have appeared in the literature. Sivaram [9] reported ionic polymerization of α-methylstyrene and β-pinene in the presence of polymer-protected $AlCl_3$, which was first found by Neckers [8]. Unfortunately, the efficiency of the polymerization catalyst was inferior. In this paper we report on the cationic polymerization of α-methylstyrene in the presence of the polystyrene-gallium trichloride complex catalyst, the preparation of which was previously reported by us [10].

EXPERIMENTAL

Materials

All solvents and the monomer used in this study were thoroughly dried, purified by standard procedures, and freshly distilled under nitrogen prior to use. Other reagents, for example, gallium trichloride (SP, anhydrous), 2,2,6,6-tetramethyl-4-hydroxypiperidinooxy free radical (AR, Aldrich Co.), and cross-linked polystyrene beads (containing 5% divinylbenzene, 16-50 mesh), were commercial reagents used without further purifying.

Preparation and Analysis of Polymer-Supported Catalyst

A polymer-supported Lewis acid catalyst, polystyrene-gallium trichloride complex, was prepared by a method described previously [10]. The chlorine content of the complex was determined by the volumetric method and by the ionic-selective electrode method, and the amount of $GaCl_3$ complexed in the polystyrene beads was calculated from the chlorine content.

Polymerization of α-Methylstyrene

Polymerizations of α-methylstyrene were carried out in the presence of the polystyrene-gallium trichloride complex (PS-$GaCl_3$) with and without solvents. The general procedures are illustrated below for a bulk polymerization.

The PS-$GaCl_3$ complex beads (0.2 g) were added to α-methylstyrene (MS) monomer (10 mL). The mixture was agitated by an electromagnetic stirrer for 3-4 h at room temperature. A white powder of poly(α-methylstyrene) was obtained by precipitating the reaction mixture in methanol and dried *in vacuo* at 50°C for 72 h. Conversions were determined by direct weighing.

In order to test for the type of the polymerization, 2,2,6,6-tetramethyl-4-hydroxypiperdinooxy free radical (3 mg), a free-radical trapping reagent, was added to a polymerization system containing MS monomer (15 mL) and PS-$GaCl_3$ complex beads (0.2 g), and the reaction was carried out at room temperature for 4 h.

Polymerization Kinetics

Bulk polymerizations of MS monomer (15 mL) in the presence of PS-$GaCl_3$ complex beads (0.2, 0.4, 0.6, 0.8, and 1.0 g) were carried out at 25°C. Solution polymerizations of MS monomer (5, 7.5, 10, and 12 mL) in the presence of PS-$GaCl_3$ complex beads (0.6 g) and CCl_4 (10, 7.5, 5, and 3 mL) were carried out at 25°C. Bulk polymerizations of MS monomer (15 mL) in the presence of PS-$GaCl_3$ complex beads (0.4 g) were carried out at -17, 0, 23, and 30°C. All conversions were determined by direct weighing after precipitating the reaction mixture (1 mL) in methanol and drying.

Effect of Solvents on the Polymerization

Solution polymerizations of MS monomer (10 mL) were carried out at 25°C in the presence of PS-$GaCl_3$ complex beads (0.4 g) and solvents (5 mL) such as CH_2ClCH_2Cl, CH_2Cl_2, CCl_4, and their mixtures (CH_2Cl_2/CCl_4 at 1/4, 1/1, and 4/1 v/v).

Measurement of Polymer Properties

Viscosities of dilute solutions of the polymers in benzene were measured with an Ubbelohde viscometer at 25.0°C. The molecular weights were estimated by the relationship given by Jordan [13],

$$[\eta] = 0.0115 + 1.93 \times 10^{-5} M_v, \tag{1}$$

and were also measured by gel permeation chromatography (GPC) (Waters Model 201) in tetrahydrofuran (THF).

Glass-transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) with a Du Pont Model 1090 thermal analysis instrument.

RESULTS AND DISCUSSION

Polystyrene-Gallium Trichloride Complex as Initiator

The polymer-supported Lewis acid catalyst, polystyrene-gallium trichloride complex (PS-$GaCl_3$), appears in all respects identical with the one previously reported [10] since these complexes showed a characteristic UV band at 470 nm and IR bands at 1500-1600 cm^{-1}, and catalyzed organic reactions with good yields.

The chlorine content of the PS-$GaCl_3$ complex beads is 3.09%, equivalent to 0.287 mmol $GaCl_3$/g of complex beads.

PS-$GaCl_3$ Complex Catalyzed Polymerization of α-Methylstyrene

1. Conversion

The conversion for bulk polymerization in the presence of the PS-$GaCl_3$ complex beads was 81.4% in 4 h at 25°C. The conversion for the solution polymerization was 87.6% in 4 h at 25°C (CH_2Cl_2 as solvent). These conversions are suitably high for industrial purposes.

2. Type of Polymerization

In the polymerization system containing a free-radical trapping reagent (2,2,6,6-tetramethyl-4-hydroxypiperidinooxy free radical), the conversion of monomer (MS) in the presence of PS-$GaCl_3$ was 13.4% in 30 min at 25°C. This is evidence that the polymerization of MS monomer with PS-$GaCl_3$ at 25°C is not a radical polymerization because the free-radical trap has no effect on the polymerization. Furthermore, the polymerization of the absolute anhydrous MS monomer in the presence of PS-$GaCl_3$ at 25°C was difficult to carry out, but a little water or halohydrocarbon would start up the polymerization. Hence, we believe that the polymerization of MS monomer with PS-$GaCl_3$ initiator is a cationic polymerization.

3. Properties of the Polymer

The weight-average molecular weight ($\bar{M}_w$) of the polymer obtained from bulk polymerization of MS monomer was 4.2×10^5 and the heterogeneity factor ($\bar{M}_w/\bar{M}_n$) was 3.8 (by GPC in THF).

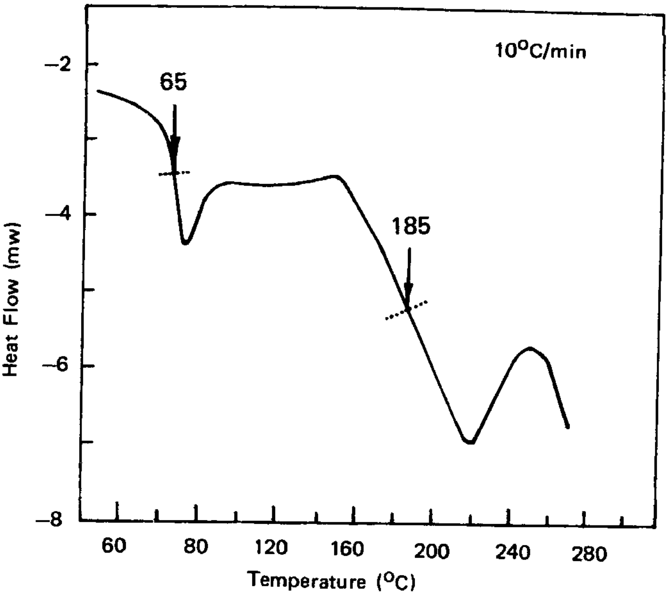


FIG. 1. DSC trace of a sample of poly(α-methylstyrene).

The glass-transition temperature (T_g) of the polymer was estimated by DSC to be 185°C (Fig. 1). This is similar to the value reported in the literature [11]. However, it must be pointed out that there is an endothermic bend at 65°C, near the ceiling temperature for polymerization of MS [11]. It must be the result of thermal depolymerization of a little poly(α-methylstyrene) caused by possible impurities. Thus, if a good plastic material is desired, the polymer must be purified or be modified by chemical or physical methods.

In summary, the polymerization of MS monomer in the presence of PS-$GaCl_3$ complex was successful; high conversions of MS monomer and high molecular weight polymers were obtained at room temperature. In common cationic polymerizations, however, high molecular weight polymer can be obtained only at very low temperature, such as -100°C. Thus, this technical improvement may be very attractive to the polymer industry.

Polymerization Kinetics

1. Relationship between Polymerization Rate and Catalyst Concentration

The plot of polymerization rates (R_p) against the initiator concentrations (C_{cat}) in Fig. 2 is evidence that R_p is proportional to C_{cat}.

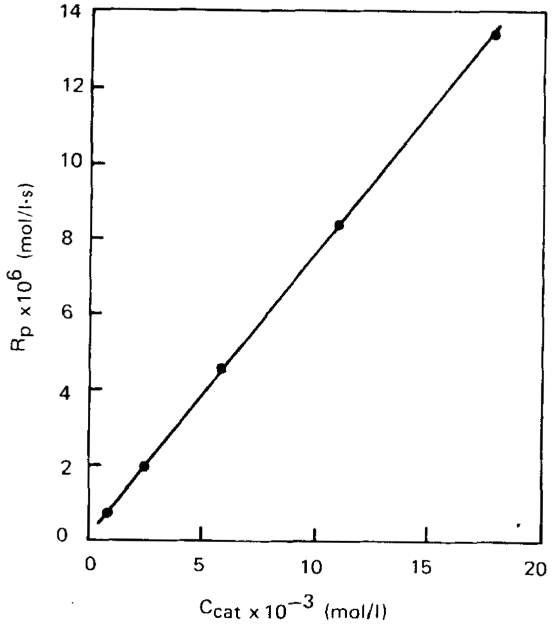


FIG. 2. Relationship between polymerization rate (R_p) and catalyst concentration (C_{cat}).

2. Relationship between Polymerization Rate and Monomer Concentration

In the solution polymerizations of MS monomer in CCl_4 at 25°C, the monomer concentration (C_{ms}) was varied from 2.3 to 5.4 mol/L while the catalyst concentration was kept at 11.5 mmol/L. A straight line was obtained on plotting the R_p against C_{ms}, as shown in Fig. 3, i.e., R_p is also proportional to ${C_{ms}}^{1.0}$.

To sum up, for the polymerization of MS monomer at room temperature with PS-$GaCl_3$ as the initiator, the kinetics obeyed the following equation:

$$R_p = k \cdot C_{cat} \cdot C_{ms}. \tag{2}$$

3. Effect of Temperature on Polymerization Rate

The relation between conversions and time for the bulk polymerizations of MS monomer in the presence of PS-$GaCl_3$ (7.6 mmol/L) at various temper-

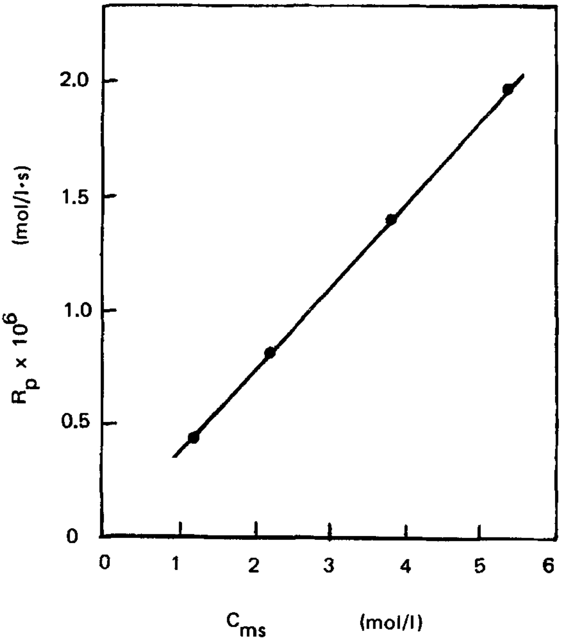


FIG. 3. Relationship between polymerization rate (R_p) and monomer concentration (C_{ms}).

atures is shown in Fig. 4. The rate constants derived by Eq. (2) are shown in Table 1. The Arrhenius plot in Fig. 5 gave an apparent activation energy (E_a) of 20.9 kJ/mol. The "collision frequency factors" (A_p) were obtained by the Arrhenius equation $k = A_p \exp(-E_a/RT)$ (Table 1).

E_a was similar to that of common cationic polymerizations, but A_p was much smaller. The A_p of common cationic polymerizations are similar to these of radical polymerizations (10^7-10^9). However, it has been reported that in cationic polymerization using I_2 as catalyst, A_p was lowered to 10^2 by the combination of the counterion I_3^- and the carbenium ion of the propagating chains [12]. In the polymerization of MS monomer using PS-$GaCl_3$, the entire complex bead can be considered as a giant counterion, and this would lead to greatly lower A_p.

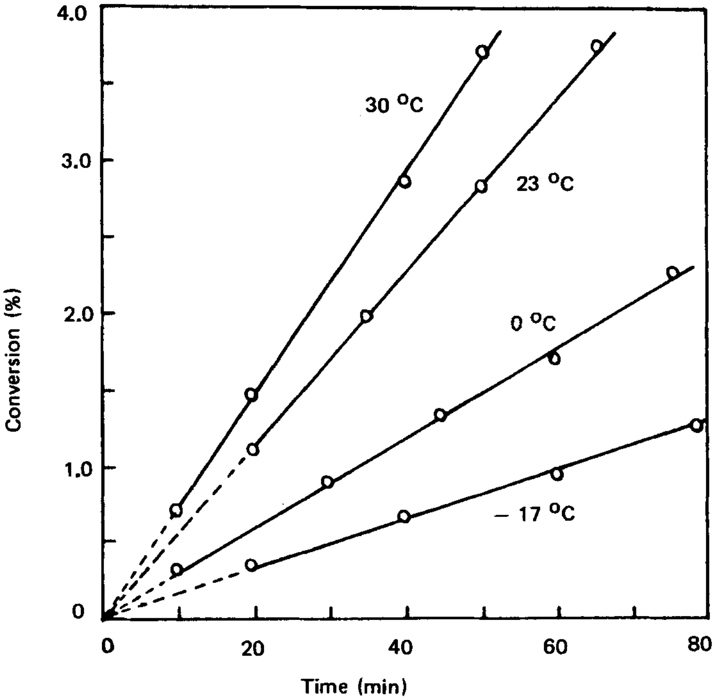


FIG. 4. Relationship between conversion and time at various temperatures.

TABLE 1. Kinetic Values at Various Temperature

Temperature, °C	Polymerization rate, $R_p \times 10^6$, mol/(L·s)	Rate constant, $k \times 10^2$, L/(mol·s)	Frequency factor, A_p, L/(mol·s)
30	4.83	1.074	26
23	3.81	0.846	24
0	1.97	0.438	23
-17	1.11	0.247	22

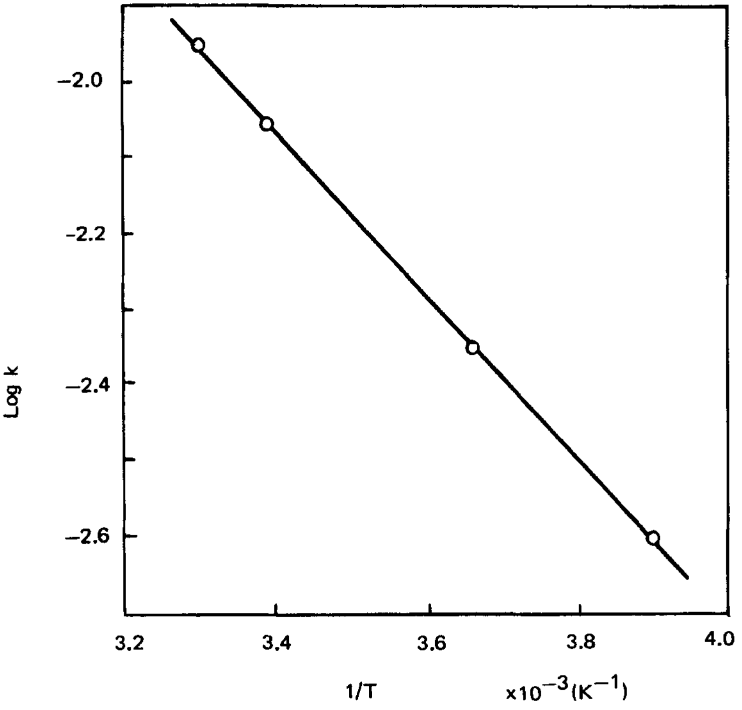


FIG. 5. Arrhenius plot for rate constants.

Effect of Solvents on Polymerization Rate

Results for the solution polymerizations of MS monomer (C_{ms} = 3.84 mol/L) with PS-$GaCl_3$ (C_{cat} = 1.15×10^{-2} mol/L) at 25°C are shown in Fig. 6 and in Table 2. A straight line was obtained by plotting R_p against ϵ (Fig. 7).

The effect of the solvent on R_p is great. R_p in the polar solvents (CH_2Cl_2 and CH_2ClCH_2Cl) was twenty times as fast as in the nonpolar solvent (CCl_4); and the higher the dielectric constant of the solvent, the higher the polymerization rate. A good linear relationship between R_p and ϵ of the solvent is an important characteristic of cationic polymerization, confirming that the polymerization of MS monomer in the presence of PS-$GaCl_3$ is a cationic polymerization.

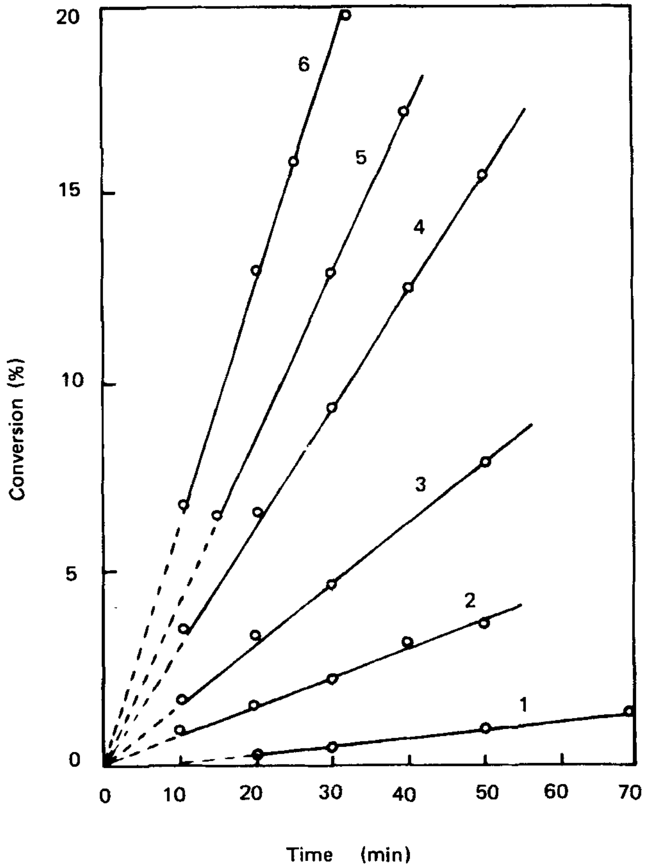


FIG. 6. Polymerization in various solvents. Numbers designate solvent systems (see Table 2).

Effect of Reaction Conditions on Polymer Molecular Weight

In common cationic polymerizations, polymers of high molecular weight can only be obtained at very low temperatures, e.g., -100°C. As a result of the low ceiling temperature for polymerization of MS monomer (61-65°C), it is difficult to obtain poly(α-methylstyrene) with high molecular weight by polymerization at higher temperature, e.g., at room temperature. For cationic polymerization at a low temperature (-100°C), it is difficult to control the

TABLE 2. Polymerization Rates and Dielectric Constants for Various Solvents

No.	Solvent system, v/v	Dielectric constant, ϵ	Polymerization rate, $R_p \times 10^5$, mol/(L·s)
1	CCl_4	2.24	0.389
2	CH_2Cl_2/CCl_4 (1/4)	3.06	1.25
3	CH_2Cl_2/CCl_4 (1/1)	5.41	2.67
4	CH_2Cl_2/CCl_4 (4/1)	7.62	5.20
5	CH_2Cl_2	9.08	7.64
6	CH_2ClCH_2Cl	10.65	9.50

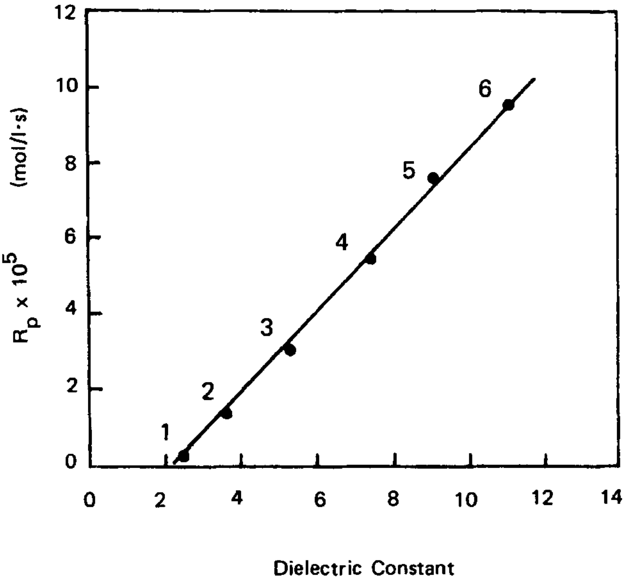


FIG. 7. Relationship between polymerization rate and dielectric constant of solvents (see Table 2).

TABLE 3. Intrinsic Viscosity and Molecular Weight of Polymers Obtained under Various Conditions

Temperature, °C	Catalyst, g/15 mL	Reaction time, h	Intrinsic viscosity, $[\eta]$, dL/g	Molecular weight,[b] $\bar{M}_v$, × 10^{-5}
23	0.2	40	11.60[a]	6.00
23	0.4	40	9.58	4.96
23	0.8	40	8.91	4.61
23	1.0	40	8.05	4.16
-17	0.4	24	9.39	4.86
12	0.4	24	7.12	3.68
30	0.4	24	6.32	3.17

[a] Result of GPC in THF, $\bar{M}_w = 2.78 \times 10^6$, $\bar{M}_w/\bar{M}_n = 3.8$.

[b] Calculated by Eq. (1).

content of cocatalyst such as water and halohydrocarbons, and because of energy costs, there have been few examples of industrial cationic polymerization so far. We hope to surmount these difficulties by using the polymer-supported Lewis acid as a cationic polymerization catalyst.

The effects of polymerization condition on the polymer intrinsic viscosity and molecular weight are shown in Table 3. It is clear that poly(α-methylstyrene) with high molecular weight could be obtained at room temperature. The molecular weight could be affected by many factors, such as the concentration of catalyst and the polymerization temperature. Although the molecular weight is lowered when the temperature is raised (Fig. 8), high molecular weight could be obtained over a wide range of polymerization temperature. This would be important for industrial production.

Polymerization Mechanism

In order to explain the experimental results, we advance a mechanism for the bulk polymerization of MS monomer in the presence of PS-$GaCl_3$ complex.

The initiation in the presence of PS-$GaCl_3$ and the cocatalyst (for example, water) to form a polymer-bound complex acid (or ion-pair). In the second step the ion-pair donates a proton to a molecule of MS monomer to give a polymer-bound new ion-pair containing carbonium ion.

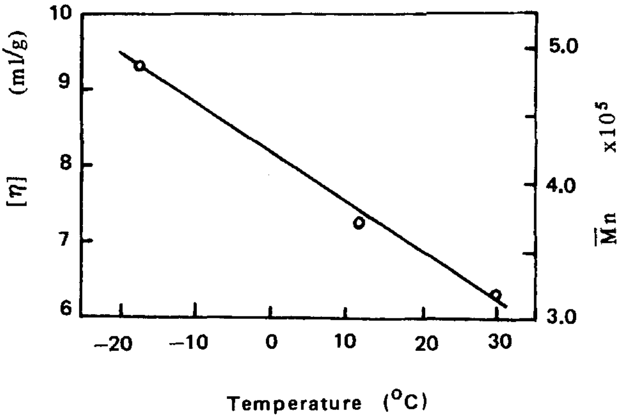
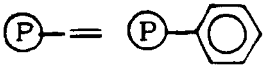
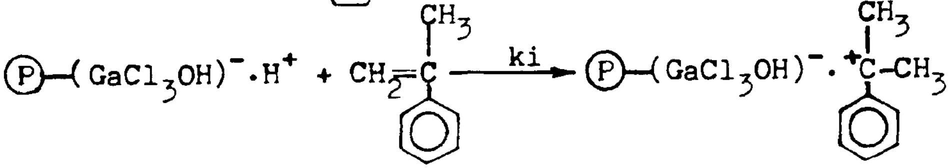


FIG. 8. Relationship between molecular weight of polymer and polymerization temperature.

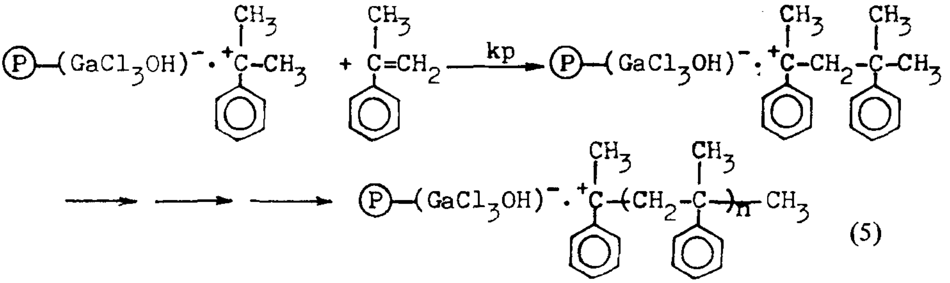
$$\text{Ⓟ}\!-\!GaCl_3 + H_2O \qquad \text{Ⓟ}\!-\!(GaCl_3OH)^- \cdot H^+ \qquad (3)$$

where 



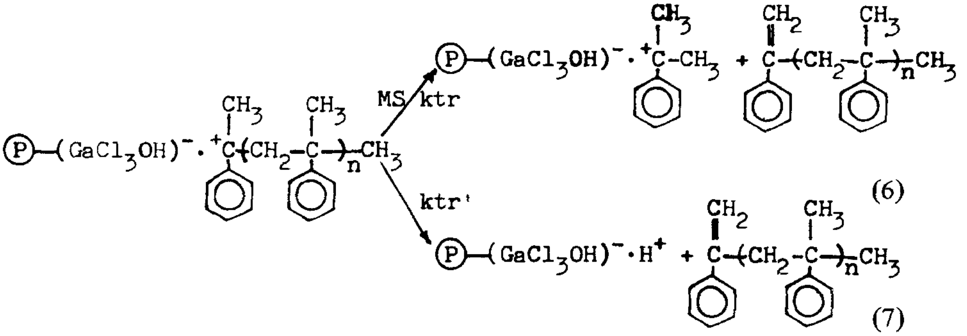
(4)

The carbonium ion then reacts with another monomer molecule by inserting into the ion-pair with the reformation of a carbonium ion at the end of each step (chain growth).



(5)

The termination reaction could take place in one of at least two ways. The ion-pair could rearrange to yield a polymer molecule with unsaturation and a complex acid (ion-pair), or the ion-pair may decompose with the liberation of the original catalyst. However, chain transfer to monomer can also be a major way of termination.



(6)

(7)

The rate equations for the main steps, (4)-(6), are

$$R_i = k_i \cdot C_{cat} \cdot C_{ms}, \tag{8}$$

$$R_p = k_p \cdot C_{ms+} \cdot C_{ms}, \tag{9}$$

$$R_{tr} = k_{tr} \cdot C_{ms+} \cdot C_{ms}. \tag{10}$$

Assuming a steady-state, $R_i = R_{tr}$, Eqs. (8) and (10) may be used to obtain C_{ms+}:

$$C_{ms+} = (k_i/k_{tr}) \cdot C_{cat}. \tag{11}$$

Thus the overall rate of polymerization is given by

$$R_p = -dC_{ms}/dt = (k_i k_p/k_{tr}) \cdot C_{ms} \cdot C_{cat} = k \cdot C_{ms} \cdot C_{cat}. \tag{12}$$

The rate equation of polymerization was found to fit the experimental results for bulk polymerization very well.

So are, few reports on the mechanism of cationic polymerization in the presence of a polymer-supported catalyst have appeared. It is well known that the general kinetic equation for cationic polymerization is $R_p = k \cdot C_m{}^a \cdot C_{cat}$, where a lies between 1 and 3, most commonly 2, because termination takes place mainly by rearrangement of the growing chains, Eq. (7), to yield a polymer molecule with terminal unsaturation. In our experiments, however, owing to greater concentration of monomer in the interstices of the crosslinked polystyrene carrier and higher polymerization temperature, chain transfer to monomer becomes significant. As a result, the kinetics takes the form of Eq. (12). On the other hand, because of the protecting action of the crosslinked polymer carrier on the growing chain, and because the beads of polymer carrier (as a very large counterion to the growing carbonium ion) greatly reduce thermal motion of the growing chain, the frequency factor (A_p) is much smaller, and termination also becomes more difficult, so that polymer of high molecular weight is obtained at room temperature.

In addition, the apparent activation energy was similar to that for common homogeneous cationic polymerizations and in the literature, because the basic processes of both the polymer-supported and the homogeneous polymerizations are similar.

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