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Registry No. K^+ κ-carrageenan, 62362-84-9; Na^+ κ-carrageenan, 37359-47-0; K^+ ι-carrageenan, 62362-83-8; Na^+ ι-carrageenan, 60616-95-7; Rb^+ κ-carrageenan, 116977-52-7.

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Preliminary Kinetic Investigation on Syndiotactic Polymerization of Styrene

Leone Oliva,† Claudio Pellecchia, Patrizia Cinquina,‡ and Adolfo Zambelli*

Dipartimento di Fisica, Universita' di Salerno, I-84081 Baronissi (SA), Italy.
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ABSTRACT: This paper reports preliminary kinetic data on syndiotactic polymerization of styrene, in the presence of $Ti(OC_4H_9)_4$–methylalumoxane. The temperature coefficient of the kinetic rate constant is 8 kcal/mol. The distribution of the molecular weights is bimodal. The polymerization rate increases more than linearly with increasing monomer concentration.

Introduction

As reported in the literature,[1-3] syndiotactic polymerization of styrene can be promoted by homogeneous catalytic systems consisting of methylalumoxane (MAO) and soluble compounds of titanium or zirconium, such as tetrabenzyltitanium, tetrabenzylzirconium, cyclopentadienyltitanium trichloride, titanium(IV) alkoxides, titanium(III) acetylacetonate, etc. In this paper we report the results of a preliminary kinetic investigation concerning the title polymerization in the presence of the catalytic system titanium tetrabutoxide (TTB)–MAO in toluene. In addition, some results obtained in the presence of other syndiotactic specific catalytic systems are reported for comparison.

Experimental Section

TTB was purchased from Aldrich. MAO was prepared as previously reported[4] by reaction of $Al(CH_3)_3$ and $CuSO_4 \cdot 5H_2O$ in toluene; the solvent and the unreacted $Al(CH_3)_3$ were removed by distillation under reduced pressure and the oligomeric MAO was isolated. Toluene was distilled under nitrogen atmosphere after refluxing over potassium for 48 h. Styrene was distilled in vacuo over CaH_2 before using.

All polymerization runs were carried out by introducing sequentially the proper amounts of toluene, MAO, and styrene in 100-mL glass flasks. The flasks were immersed in an oscillating thermostatic bath and the polymerizations were initiated by injecting the required amount of TTB. Polymerization runs were stopped by injecting methanol and the polymers were coagulated with acidified methanol, recovered by filtration, washed with fresh methanol, and dried under vacuum. Polymerization conditions and results are reported in Tables I–VI. Polymer samples were fractionated by exhaustive extraction with boiling acetone. Molecular weights of the raw polymers or, where specified, of the extraction residues, were determined by GPC in 1,2-dichlorobenzene at 135 °C by using a Waters 150-C apparatus.

Table I
Yields and Molecular Weights of Polystyrenes Obtained at Increasing Times[a]

run	temp, °C	time, min	yield, mg	$\bar{M}_w$	$\bar{M}_n$
1	50	20	42	224000	11000
2	50	30	56	251000	13000
3	50	40	95	281000	16000
4	50	60	143	308000	12000
5	50	80	148	344000	29000
6	87	15	115	76000	16000
7	87	30	255	75000	8000
8	87	45	340	78000	15000
9	87	60	543	75000	8000

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; MAO, 4.0 mmol (based on Al); TTB, 4.5×10^{-5} mol.

Results and Discussion

In Table I (runs 1–5) are reported the amounts of polymer produced in a series of low-conversion polymerization runs performed at 50 °C. Under these conditions, the yield of polymer increases linearly with increasing reaction time, showing that the activity of the catalyst is

* To whom correspondence should be addressed.
† Dipartimento di Chimica, via Mezzocannone 4, I-80134 Napoli, Italy.
‡ Present address: Istituto G. Donegani, via Fauser 4, I-28100 Novara, Italy.

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Table II
Yields and Molecular Weights of Polystyrenes Obtained at Increasing Monomer Concentration[a]

run	$[C_8H_8]$, mol/L	yield, mg	insol fractn,[b] %	$\bar{M}_w$[c]	$\bar{M}_n$[c]
10	1.57	128	81	316 000	86 000
11	2.62	241	83	441 000	101 000
12	3.15	402	85	494 000	144 000
13	3.67	441	84	487 000	95 000
14	4.20	533	85	568 000	133 000
15	5.25	788	80	567 000	138 000

[a] Polymerization conditions: T = 50 °C; time = 100 min; MAO, 5.6 mmol (based on Al); TTB, 4.5 × 10^{-5} mol; for all runs total volume was 40 mL, using the proper amount of toluene. [b] In boiling acetone. [c] Of the insoluble fraction.

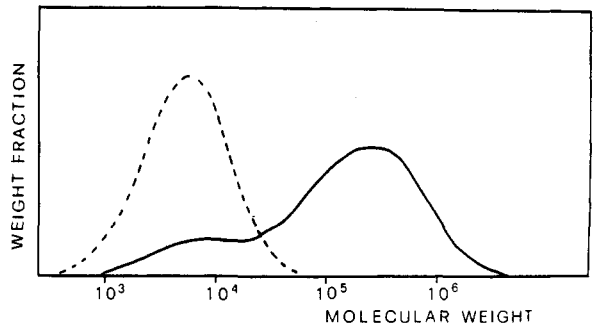

Figure 1. Molecular weight distribution determined by GPC of the polystyrene obtained in run 5 (solid line) and the polystyrene obtained in similar polymerization conditions in the presence of tetrabenzylzirconium and MAO (dotted line).

constant at least for a fairly long time. Similar results have been obtained even at substantially higher temperature (see Table I, runs 6–9). The ratio between the amount of polymer produced at short times and the number-average molecular weights (i.e., the moles of macromolecules) represents the upper limit of the molar amount of the catalytic complex, which appears to be less than 10% of the TTB used in the polymerization runs. The concentration of the catalytic complexes is close to that previously found for the catalytic system tetrabenzyltitanium–MAO.[5]

At 50 °C the average molecular weights also increase, although less than linearly, with polymerization time. At higher temperature (87 °C) a stationary value of $\bar{M}_w$ is reached soon after the beginning (see Table I). These results are consistent with the presence of chain-transfer processes, such as β-hydrido abstraction, already demonstrated in a previous paper,[6] in the presence of the catalytic systems tetrabenzyltitanium or tetrabenzylzirconium and MAO. The distribution of molecular weights is very broad, especially for the raw polymers, which contain some atactic low molecular weight material soluble in acetone, in addition to the syndiotactic fraction. However, even for the syndiotactic acetone-insoluble fractions, the $\bar{M}_w/\bar{M}_n$ ratio is larger than that predicted by the Schultz-Flory equation, which is obeyed by the polymer prepared in the presence of other catalysts, e.g., tetrabenzylzirconium–MAO (see Figure 1). Table II shows that under the reported experimental conditions, the amount of polymer produced at constant reaction time increases more than proportionally with monomer concentration. At this stage a tentative explanation, which may possibly be later confirmed, may be coordination of the monomer before insertion, in competition with coordination of the aromatic solvent (toluene). As a matter of fact, a plot of the reciprocal of the conversion versus the reciprocal of the monomer concentration is a straight line (see Figure 2). This type of dependence could be justified, as reported in

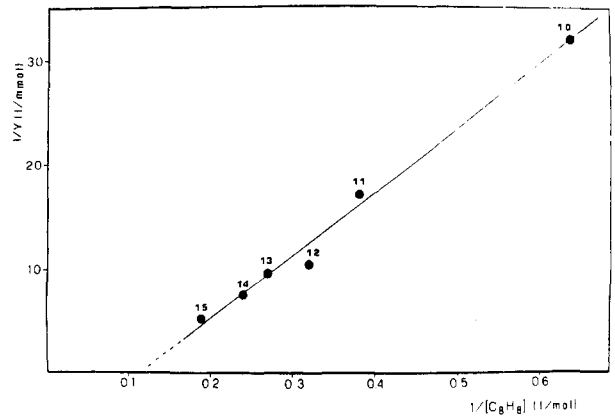

Figure 2. Linear relationship between the reciprocal of the monomer concentration and the reciprocal of the yield. The numbers in the figure refer to the runs reported in the tables.

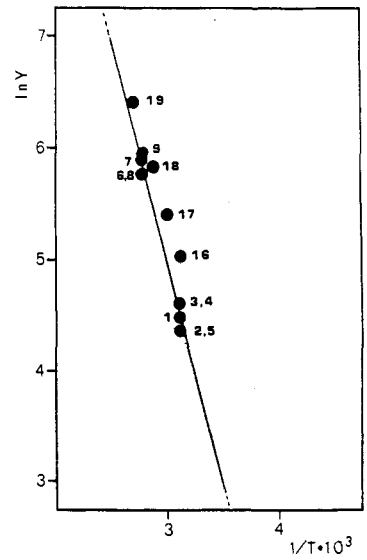

Figure 3. Plot of the natural logarithms of the yield of polystyrene versus the reciprocal of the absolute temperature. The numbers in the figure refer to the runs reported in the tables.

the Appendix, by considering, as an example, the following coordination and insertion steps

$$C^*\text{-}(C_8H_8)_n\ldots + C_7H_8 \overset{K_T}{\rightleftharpoons} C_7H_8\cdot C^*\text{-}(C_8H_8)_n\ldots \quad (1)$$

$$C^*\text{-}(C_8H_8)_n\ldots + C_8H_8 \overset{K_S}{\rightleftharpoons} C_8H_8\cdot C^*\text{-}(C_8H_8)_n\ldots \quad (2)$$

$$C_8H_8\cdot C^*\text{-}(C_8H_8)_n\ldots \xrightarrow{k_i} C^*\text{-}(C_8H_8)_{n+1}\ldots \quad (3)$$

where $C^*\text{-}(C_8H_8)_n\ldots$ is the catalytic complex with n = polymerization degree of the growing chain, K_T and K_S are the equilibrium constants for the coordination of toluene and styrene, respectively, and k_i is the kinetic rate constant for the insertion of the monomer into the metal–polymer bond, and by considering that the molar volumes of toluene and styrene are very similar so that the sum of the molar concentrations of the monomer and the solvent is approximately constant in the runs reported in Table II. It is also found that the average molecular weight increases with increasing monomer concentration.

In Figure 3 the logarithm of the polymer yield is plotted against the reciprocal of the absolute temperature for the runs reported in Table III, all of which were performed under identical conditions except for the polymerization temperature. The conversions obtained in runs 1–9, Table I, are also reported after normalization to constant reaction time (100 min). The value found for the temperature

Table III
Yields and Molecular Weights of Polystyrenes Obtained at Increasing Temperature[a]

run	temp, °C	yield, mg	insol fractn,[b] %	$\bar{M}_w$[c]	$\bar{M}_n$[c]
16	48	150	83	578000	162000
17	60	223	86	361000	98000
18	75	343	94	148000	44000
19	92	605	89	85000	25000

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; MAO, 1.9 mmol (based on Al); TTB, 1.9×10^{-5} mol; time, 100 min. [b] In boiling acetone. [c] Of the insoluble fraction.

Table IV
Yields and Molecular Weights of Polystyrenes Obtained at Increasing Concentration of MAO[a]

run	[MAO],[b] mol/L	yield, mg	insol fractn,[c] %	$\bar{M}_w$[d]	$\bar{M}_n$[d]
20	0.0096	20	0		
21	0.030	222	87	578000	159000
22	0.090	194	86	427000	102000
23	0.270	185	70	257000	56000

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; TTB, 1.2×10^{-5} mol; T = 50 °C; time = 100 min. [b] Based on Al. [c] In boiling acetone. [d] Of the insoluble fraction.

coefficient is 8 kcal/mol. This coefficient includes the activation energy of chain propagation, the energies involved in the formation of the catalytic complexes from the cocatalysts, and the energies of possible termination reactions.

Table IV reports the results of polymerization runs performed with increasing concentrations of MAO. The amount of polymer produced depends very little on the concentration of MAO provided that the [MAO]/[TTB] ratio is larger than 50. At very low ratios a small amount of stereoirregular polymer is produced. The molecular weights decrease with increasing [MAO], indicating some chain transfer to MAO itself or even to the $Al(CH_3)_3$ accompanying the MAO. In fact, a decrease of molecular weight of the polymer produced is observed when a small amount of $Al(CH_3)_3$ is added to the catalytic system.[7]

At constant MAO concentration, the amount of polymer produced reaches a maximum and then decreases with increasing concentration of TTB (see Table V). The molecular weight and the fraction of polymer insoluble in boiling acetone also reach a maximum and then decrease with increasing concentration of TTB.

When the concentration of *both* TTB and MAO are increased ([MAO]/[TTB] = 100) the polymer yield increases, reaching an almost constant value, at least in the range of practical concentrations of catalyst (see Table VI). The amount of polymer insoluble in boiling acetone in the different runs is indicative of the overall stereospecificity of the polymerization. In fact the insoluble fractions are highly syndiotactic while the soluble ones are stereoirregular except when the molecular weight is unusually low.

Conclusions

The data reported in this paper are still preliminary and were collected in order to allow us to draw basic conclusions concerning the nature of the polymerization mechanism. However, the dependence of the polymerization rate on the concentration of titanium and MAO seems to show that the formation of the catalytic complexes, by interaction of the cocatalysts, follows a rather complicated pattern. The temperature coefficient of the polymerization

Table V
Yields and Molecular Weights of Polystyrenes Obtained at Increasing Concentration of TTB[a]

run	[TTB], mmol/L	yield, mg	insol fractn,[b] %	$\bar{M}_w$[c]	$\bar{M}_n$[c]
24	0.10	143	65	328000	64000
25	0.30	256	75	369000	102000
12	0.92	402	85	494000	144000
26	2.75	515	85	421000	63000
27	6.75	101	55	407000	60000
28	8.25	73	30	394000	59000

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; MAO, 5.6 mmol (based on Al); T = 50 °C; time = 100 min. [b] In boiling acetone. [c] Of the insoluble fraction.

Table VI
Yields of Polystyrenes Obtained at Increasing Concentration of TTB and MAO[a]

run	[TTB], mmol/L	[MAO],[b] mmol/L	yield, mg	insol fractn,[c] %
29	0.15	15	130	93
30	0.30	30	273	95
31	0.62	62	655	89
32	1.25	125	611	89
33	2.5	250	590	85

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; T = 50 °C; time = 100 min. [b] Based on Al. [c] In boiling acetone.

rate constant is in the usual range for hydrocarbon monomers.

The average lifetime of the macromolecules decreases while increasing the polymerization temperature.

Finally, the dependence of the polymerization rate from the monomer concentration suggests competitive coordination of the monomer and the aromatic solvent on the catalytic complexes.

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Appendix

The proportionality between the reciprocal yields ($1/Y$) and the reciprocal molarities of the monomer ($1/[C_8H_8]$) observed in Figure 2 for runs 10–15 of Table II could be justified by considering that (1) as mentioned in the text, the yields are proportional to the polymerization rates (R), (2) the sum of the molarity of the monomer ($[C_8H_8]$) and that of the solvent ($[C_7H_8]$) is the same in all the runs

$$[C_8H_8] + [C_7H_8] = \bar{A} \tag{4}$$

(3) all the runs have been performed in the presence of the same amount of catalyst, at the some temperature, and at constant total volume and by assuming, e.g., (1) competitive coordination of the solvent and the monomer according to the equilibria 1 and 2, as reported in the text and (2) insertion of the coordinated monomer on the bond between C* and the growing chain according to eq 3.

As a consequence

$$Y \propto R = k_i[C_8H_8\cdot C^*\text{–}(C_8H_8)_n\ldots] \tag{5}$$

With the usual assumptions for polyinsertion reactions, i.e., that K_T, K_S, and k_i are independent of n and that for all the considered runs

$$\sum_{n=0}^{\infty}[C^*\text{–}(C_8H_8)_n\ldots] + \sum_{n=0}^{\infty}[C_8H_8\cdot C^*\text{–}(C_8H_8)_n\ldots] + \sum_{n=0}^{\infty}[C_7H_8\cdot C^*\text{–}(C_8H_8)_n\ldots] = \bar{B} \tag{6}$$

one can derive, from eq 5 with obvious substitutions, eq 7

$$\frac{1}{Y} \propto \frac{1}{R} = \frac{1 + K_T\bar{A}}{k_i K_S \bar{B}} \frac{1}{[C_8H_8]} + \frac{K_S - K_T}{k_i K_S \bar{B}} \quad (7)$$

Registry No. TTB, 5593-70-4; styrene, 100-42-5; polystyrene, 28325-75-9.

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Electron-Transfer Reaction of Macromolecular Cobalt(III) Complex with $[Ru(NH_3)_6]^{2+}$. Effect of Microenvironment Occupied by Polymer Backbone

Yoshimi Kurimura* and Takashi Kikuchi

Department of Chemistry, Ibaraki University, Mito, Ibaraki 310, Japan

Eishun Tsuchida

Department of Polymer Chemistry, Waseda University, Shinjuku-ku, Tokyo 160, Japan.

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ABSTRACT: The rates and kinetic parameters of the electron-transfer reaction of the polymer-bound Co(III) complex *cis*-$[Co(en)_2PVP(N_3)]^{2+}$ (PVP = poly(4-vinylpyridine), en = ethylenediamine) with $[Ru(NH_3)_6]^{2+}$ were determined in aqueous solutions of sodium perchlorate and sodium chloride and a water–ethanol mixture at pH 2. The electron-transfer rate of the polymer–metal complex was found to be very sensitive to the type of dissolved anion at a given ionic strength. Higher reactivity of the polymer–metal complex in perchlorate solution than in chloride solution may be ascribed to partial dehydration of the pendant Co(III) moieties and the $[Ru(NH_3)_6]^{2+}$ ions in the microenvironment of the polymer backbone. The lower activation enthalpy of the electron-transfer reaction seems to be attributable to the higher reactivity of the polymer–metal complex in perchlorate solution.

Despite the considerable experimental and theoretical studies of electron-transfer reactions of common metal complexes, there are few data on those of synthetic macromolecule–metal complexes.[1-7] Aquochromium(II) reduction of polypeptide–amminecobalt(III) complex, obtained by reaction of aquopentaamminecobalt(III) perchlorate with poly(glutamic acid), has been reported.[1,2] The results of detailed investigation suggested that there may be two parallel reactions: the faster and slower processes ascribed to the reduction of acidotetraamminecobalt(III) and (carboxylato)aquotetraamminecobalt(III), respectively.[2] The results of kinetic studies on the redox reactions of polycation-bound Co(III) complexes and anionic iron(II) complexes indicated that the most important factor governing the rate is Coulombic interaction.[3-7]

Investigation of the electron-transfer reactions of polycationic macromolecule–metal complexes with positively charged low molecular weight metal complexes are important since the results of such investigations would confer a wider understanding of the factors that govern the rate of electron-transfer of macromolecule–metal complexes. We report here the electron-transfer reaction of a polycationic macromolecule Co(III) complex, *cis*-$[Co(en)_2PVP(N_3)]^{2+}$ (en = ethylenediamine and PVP = poly(4-vinylpyridine)), with $[Ru(NH_3)_6]^{2+}$. We have found that (i) the repulsive force between the polycation of the Co(III) complex and $[Ru(NH_3)_6]^{2+}$ ion is not an important factor in controlling the reaction rate and (ii) the reaction rate is very sensitive to the type of dissolved anions in the polymer complex system.

Experimental Section

General Procedures. Poly(4-vinylpyridines) (PVP) having a degree of polymerization (Pn) of 98 and 19 were used as the polymeric ligands. Partially quarternized poly(4-vinylpyridine), quarternized by ethyl bromide (QPVP), was prepared by the reaction of the PVP of Pn = 98 with ethyl bromide in ethanol. $[Ru(NH_3)_6]Br_2 \cdot 6H_2O$ was prepared and analyzed according to the published procedure.[8] The method of preparation of *cis*-$[Co(en)_2PVP(N_3)]Cl_2$ and *cis*-$[Co(en)_2Py(N_3)]Cl_2$ (Py = pyridine)[9,10] has been described in the literatures cited. Degrees of coordination (x) of the Co(III) complexes for the $[Co(en)_2PVP(N_3)]Cl_2$ prepared were 0.39 for the PVP of Pn = 98 and 0.47 for the PVP of Pn = 19. The concentration of the polmer-bound Co(III) complex is represented by that of the monomeric Co(III) unit. Viscosity measurements were carried out in aqueous solutions with an Ubbelode type viscometer at (25 ± 0.1) °C. A solution of $[Ru(NH_3)_6]^{2+}$ was prepared by reduction of $[Ru(NH_3)_6]Br_3$ solution with amalgamized zinc. Concentrations of the Ru(II) were determined by reduction of a standard solution of $[Co(NH_3)_5]Cl_2$.

Kinetic Experiments. Rates of electron transfer were measured in dilute acid solutions at pH 2.0. Values of pH and ionic strength in the reaction solutions were adjusted with hydrochloric acid and sodium chloride or perchloric acid and sodium perchlorate. The former and latter cases will hereafter be described simply as a "chloride system" and a "perchlorate system", respectively. The reaction was initiated by mixing the solutions of Co(III) with those of Ru(II) by using a mixing apparatus (Union Gikken MX 7). All the reactions were followed with the Ru(II) in large excess, as required for pseudo-first-order kinetics. The initial concentration of the Co(III) and Ru(II) were 2.5×10^{-4} and $(2.5–6.0) \times 10^{-3}$ M, respectively. Reactions were followed by disappearence of the Co(III) absorption in the 510-nm region using a Hitachi Model 320 recording spectrometer. The second-order rate constants (k) were obtained from the slopes of the log ($A_t - A_\infty$) vs reaction time plots where A_t and A_∞ are the absorbances at time t and after all the Co(III) had been reduced to Co(II), respectively.

Results and Discussion

The chemical structure and analytical data of *cis*-$[Co(en)_2PVP(N_3)]Cl_2 \cdot nH_2O$ are shown in Figure 1 and Table I, respectively. Otherwise noted, the polymer Co(III)–PVP complex having the PVP with a degree of polymerization of 98 was used for the experiments. *cis*-$[Co(en)_2Py(N_3)]Cl_2$ was used as the corresponding low molecular weight ana-

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