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Metal-Containing Initiator Systems

31. Vinyl Polymerization with Ferrocene-Acid Anhydride Systems

Yang-un Mun and Takayuki Otsu

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

SUMMARY

The polymerization of vinyl monomers with the initiator systems of ferrocene and acid anhydrides were investigated. The initiator activity for radical polymerization of methyl methacrylate(MMA) was higher than that for styrene(St). However, isobutyl vinyl ether was not polymerized. The rate of polymerization of MMA with ferrocene/benzoic anhydride system was in proportional to the square root concentrations of both compounds of the initiator system, indicating the mechanism of radical polymerization. When an alternating copolymer of ethylene with maleic anhydride was used as an acid anhydride, a graft copolymer, which was soluble in dimethylformamide and tetrahydrofuran, was produced from radical polymerization of MMA.

INTRODUCTION

In previous papers of this series, it was found that some transition metals and their σ- and π-complexes such as hydrogenation metal catalysts(1~4), metal acetylacetonates(5~7), metallocenes(8~10) and bisbenzenechromium(8), could induce selectively radical and ionic polymerizations in the presence or absence of alkyl halides. Especially, bisbenzenechromium(8), cobaltocene(11) or nickelocene(9) induced the coordination polymerization of acrylonitrile, but its combined systems with benzyl bromide initiated both radical polymerizations of styrene(St) and methyl methacrylate(MMA) as well as the cationic polymerization of isobutyl vinyl ether.

Recently, some metallocenes were found to form initiator systems with acid anhydrides instead of alkyl halides(8~10). The present paper describes the results obtained in vinyl polymerizations initiated by the ferrocene/acid anhydrides systems.

EXPERIMENTAL

Materials. Ferrocene was synthesized according to Little's method(12), and recrystallized from methylene dichloride and ligroin, followed by sublimation.

Acetic anhydride was used after distillation on phosphorus pentaoxide. Succinic anhydride and maleic anhydride were recrystallized from anhydrous ethanol and chloroform, respectively. Commercial benzoic anhydride and phthalic anhydride were used without further purification. Polymeric acid anhydride was prepared by the alternating copolymerization of ethylene with maleic anhydride(13).

MMA, St and isobutyl vinyl ether(IBVE) were purified by ordinary methods, and distilled in a stream of nitrogen before use. Solvents and other reagents were also used after purifications.

Polymerization procedure. Polymerization was carried out in a sealed tube without diffused light under shaking in a thermostat maintained at a given temperature. After polymerization, the content of the tubes was poured into a large amount of methanol containing a small amount of concentrated hydrochloric acid. The polymer obtained was filtered off, and dried to a constant weight. The rate of polymerization was calculated from the weight of the dried polymer obtained.

Analysis of polymers. Intrinsic viscosity($[\eta]$) of poly(MMA) was determined in its dilute benzene solution at 30°C, and the number-average molecular weight ($\bar{M}_n$) was calculated from the reported equation(14).

The composition of the copolymers was determined by elementary analysis. The formation of graft copolymer was confirmed by IR spectrum and GPC.

RESULTS AND DISCUSSION

Initiator Activities. The results of polymerizations of vinyl monomers with the ferrocene/acid anhydrides systems are shown in Table 1. As can be seen in this table, these initiator systems are effective for the polymerization of MMA, and the activity of the ferrocene/benzoic anhydride is almost identical to that of the ferrocene/carbon tetrachloride system(8). For the polymerization of St, these systems are also observed to serve as an initiator, but their activities are lower than those for the MMA polymerization. However, these systems do not induce the polymerization of isobutyl vinyl ether, contrary to the systems of cobaltocene or nickelocene and alkyl halide(8).

Kinetic Study of Polymerization of MMA with Ferrocene/Benzoic Anhydride System. The results obtained are shown in Fig. 1, in which this polymerization is found to proceed linearly with the time. From the plots of the rates of polymerization(R_p) with the reciprocal polymerization temperature according to the Arrehnius equation, the activation energy for this polymerization was calculated to be 66.7 kJ/mol. This value is somewhat lower than that(~80 KJ/mol) which has been found with azobisisobutyronitrile or benzoyl peroxide, and agreed with that(59.6 KJ/mol) observed for ferrocene /carbon tetrachloride system(8). From kinetic investigations of the polymerization of MMA with ferrocene/

Table 1

Results of polymerization with Ferrocene/Acid Anhydrides

Monomer	Anhydride[1)]	Solv.[1)]	Temp(°C)	Time(hr)	Yield(%)
MMA	None	Bz	90	16	1.8
MMA	AAn	-	70	2	3.7
MMA	BAn	-	70	2	3.9[2)]
MMA	PAn	-	70	2	3.5
MMA	SAn	-	70	2	2.3
MMA	MAn	-	70	2	3.2
MMA	(CCl_4)	-	70	2	4.0
St	BAn	DCE	80	12	4.4
St	BAn	Bz	80	12	5.9
St	AAn	Bz	80	17	7.9
St	PAn	Bz	80	17	8.4
St	SAn	Bz	80	17	7.3
IBVE	BAn	-	80	20	0
IBVE	PAn	-	80	20	0
IBVE	AAn	-	80	20	0
IBVE	(BzBr)	AcN	90	16	52.1

[1)] AAn:acetic anhydride, BAn:benzoic anhydride, PAn:phthalic anhydride, SAn:succinic anhydride, MAn:maleic anhydride, Bz:benzene, DCE:dichloroethane, AcN:acetonitrile. [2)] $[\eta]$= 4.09 dl/g, $\bar{M}_n$= 1.04 x 10^6.

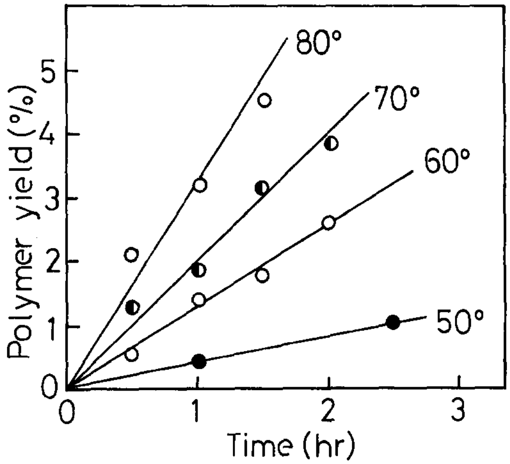


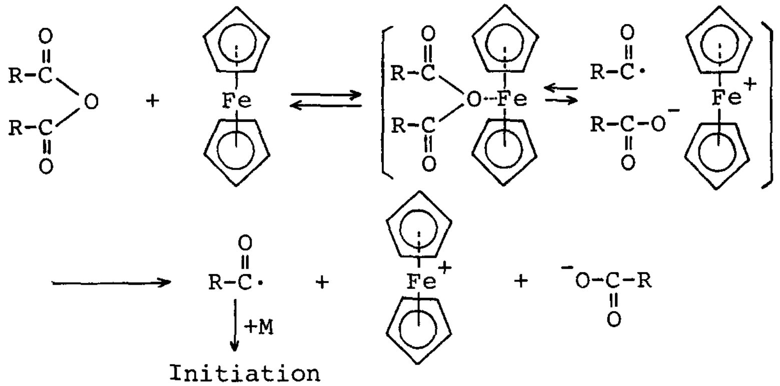
Fig. 1 Time-conversion curves for bulk polymerization of MMA; [ferrocene]=[Benzoic Anhydride]= 20 mmol/l

benzoic anhydride system at 70°C the rates of polymerization were in proportional to the square root concentrations of each initiator component and to the first order of the MMA monomer concentration. Therefore, it is clear that this polymerization is performed as follows: the initiation is induced by a radical produced from the reaction of ferrocene with benzoic anhydride, and the termination occurs bimolecularly.

To clarify further this point, the copolymerization of MMA with St was carried out at 70°C. The observed comonomer-copolymer composition curve was in agreement with that of ordinary radical copolymerization. Benzoquinone inhibited this polymerization.

Initiation Mechanism. The interaction of ferrocene with benzoic anhydride in initiation step was examined by UV spectra accoring to the Job's continuous variation method(15). The results are shown in Fig. 2. The optical densities at 410, 430 and 440 nm determined from UV spectra of various compositions of the mixture gave a maxmnm at the 1:1 mixture of ferrocene with anhydride, taken to indicate that a 1:1 charge transfer interaction is formed between them.

From this and kinetic results, the initiation mechanism by these system is assumed as follows:



Similar initiation mechanism has been presented for the cobaltocene, nickelocene and ferrocene/alkyl halide systems(10,11) and the reduced nickel/alkyl halide or acid anhydride systems(3,4).

Graft Polymerization. From the above mechanism, if polymeric anhydride is used as initiator component, a graft copolymer seems to be obtained. The results of polymerization of MMA with the ferrocene/alternating copolymer of ethylene with maleic anhydride[alt. copoly (E/MAn)] system are shown in Table 2.

From this table, no polymerization was found to occur in the absence of ferrocene, but the binary system

Table 2

Graft Polymerization of MMA with Ferrocene/Alt. Copoly-(E/MAn)1)

Alt. Copoly-(E/MAn)(g)	Fero-cene(g)	Total Yield(g)	Soluble in Bz(g)	Grafting Efficiency(%)2)
0.10	0.04	0.53	0.17	60.1
0.15	0.04	0.60	0.15	66.3
0.20	0.04	0.65	0.13	58.3
0.25	0.04	0.76	0.15	70.0
0.20	0	0.20	0	0

1) Polymerized in DMF at 70°C for 3 hours.

2) Calculated by the equation: [Poly(MMA) polymerized]-[Poly(MMA) extracted] ×100/[Poly(MMA) polymerized].

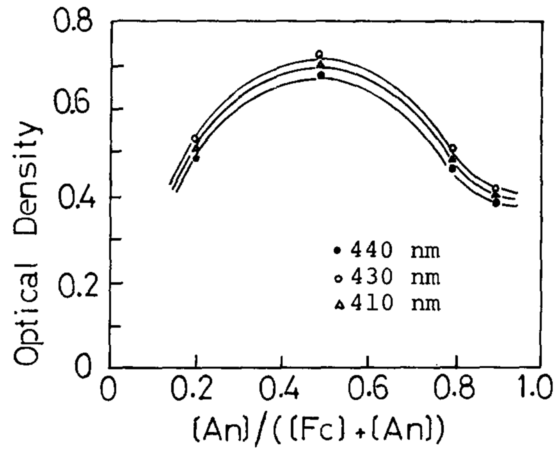


Fig. 2 Continuous variation curves for the ferrocene/benzoic anhydride(1:1 molar) mixture in benzene

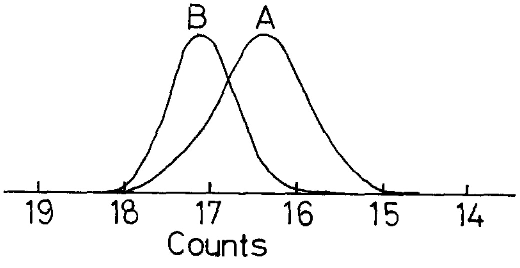


Fig. 3 GPC curves of benzene-soluble[homopoly(MMA)](A) and benzene-isoluble[graft] polymers(B)

with polymeric anhydride initiates the polymerization. The product polymer was extracted with benzene. The benzene-soluble and benzene-insoluble polymers were found to be the homopoly(MMA) and the graft copolymer, respectively. The latter graft copolymer was soluble in dimethylformamide and tetrahydrofuran.

Fig. 3 shows examples of the GPC curves of the benzene-soluble and benzene-insoluble polymers in tetrahydrofuran. From this figure, the molecular weight distribution curve of the graft copolymer was found to shift to the high molecular weight side as compared with that of the homopoly(MMA) extracted. The formation of the graft copolymer is considered to occur according to the initiation mechanism stated above.

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