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Acrylonitrile Copolymers Using Cobalt Acetylacetonate Triethylaluminum Initiator System. IV. Copolymerization with Styrene*

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ABSTRACT

The copolymerization of acrylonitrile with styrene was studied using homogeneous Ziegler-Natta initiator containing cobalt acetylacetonate and triethylaluminum in benzene at 50°C. The overall rate of polymerization shows an interesting dependence on triethylaluminum, monomer, and initiator concentrations. The overall activation energy for the polymerization was found to be 10 kcal/mol. The polymerization was susceptible to inhibition by added hydroquinone. These observations are explained based on a mechanism wherein acrylonitrile competes for complexation with both the catalyst sites and the Lewis acid. The catalyst sites appear to possess both coordinate anionic and free radical characteristics.

INTRODUCTION

Homogeneous Ziegler-Natta catalysts based on transition metal acetylacetonates and alkylaluminum compounds are known to polymerize

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α-olefins at low temperatures [1]. We have recently shown that cobalt acetylacetonate triethylaluminum is an efficient initiator for the copolymerization of acrylonitrile with vinyl acetate [2].

In this paper we report our results of the study of copolymerization of acrylonitrile with styrene using cobalt acetylacetonate-triethylaluminum initiator system. Prior to this study there has been only one report of the copolymerization of styrene and acrylonitrile using a Ziegler-Natta catalyst system; namely, vanadium oxychloride and triisobutylaluminum in n-hexane at 40°C [3]. The catalyst was shown to produce an equimolar alternating copolymer.

EXPERIMENTAL

Materials

Styrene and acrylonitrile were washed free of inhibitors, dried, and distilled under nitrogen. Cobalt acetylacetonate was prepared by a procedure reported [4]. Triethylaluminum (Ethyl Corp., U.S.A.) was used as such. All monomer and catalyst additions were performed in a dry box which was continuously flushed with a stream of high purity nitrogen.

Copolymerization Procedure

Dry benzene ($<$ 10 ppm water), cobalt acetylacetonate, and a mixture of monomers were placed in a 50-mL Erlenmeyer flask. The required amount of triethylaluminum was added as 0.5 M solution in benzene and the flask was tightly stoppered. The flask was then placed in a constant temperature bath at 50°C. After the proper reaction time had elapsed, the polymer was precipitated using acidified methanol, filtered, and dried. The copolymers were purified by dissolving in DMSO and reprecipitated using methanol.

Characterization of Copolymers

Elemental analysis was performed on a Coleman model 33 analyzer. IR spectra were recorded on a Beckman 4220 and NMR spectra on a JEOL JNM FX-100 instrument. GPC analysis was performed using a Waters Associates Model AIC/GPC 244 instrument with standard μ-Styragel columns. Intrinsic viscosity was determined using a Ubbelhode viscometer in DMF at 35°C.

RESULTS AND DISCUSSION

Cobalt acetylacetonate or triethylaluminum alone did not initiate copolymerization of acrylonitrile with styrene at 50°C. However, in combination they were effective initiators of copolymerization. As observed earlier, the order of addition of the initiator components had a profound effect on copolymerization efficiency [2]. It appears that the preparation of the active initiator complex in the presence of monomer is an essential prerequisite for copolymerization.

The fact that the polymers isolated were true copolymers was ascertained by a number of independent methods, such as elemental analysis, solubility, GPC, and ^{13}C-NMR. The copolymers were found to be only partially soluble in benzene but fully soluble in DMF, DMSO, etc. The soluble portions in benzene as well as in DMSO showed an identical acrylonitrile content (38-40 mol%). Gel permeation chromatography of copolymers in DMF showed a single peak and were significantly displaced on the elution time scale from homopolymers of similar molecular weight ranges. The MWD of copolymer samples prepared by using Co(acac)$_3$-Et$_3$Al at 40°C was 2.7 (based on a calibration using standard polystyrene samples). The ^{13}C-NMR showed similar triad distribution and carbon assignments as reported for styrene acrylonitrile copolymer prepared by free radical polymerization techniques [5]. The intrinsic viscosity of copolymer prepared by Co(acac)$_3$-Et$_3$Al (0.2 dL/g) was, however, lower than that obtained using AIBN (0.7 dL/g).

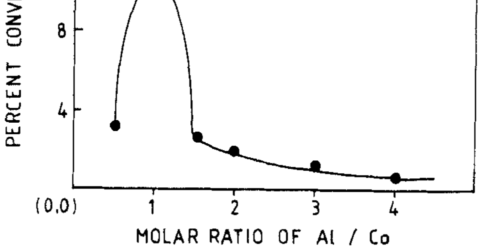

FIG. 1. Effect of Al/Co ratio on conversion using the Co(acac)$_3$-Et$_3$Al initiator system. [Co(acac)$_3$] = [Et$_3$Al] = 0.05 M, [ST] = [AN] = 4 M, 50°C, 1 h.

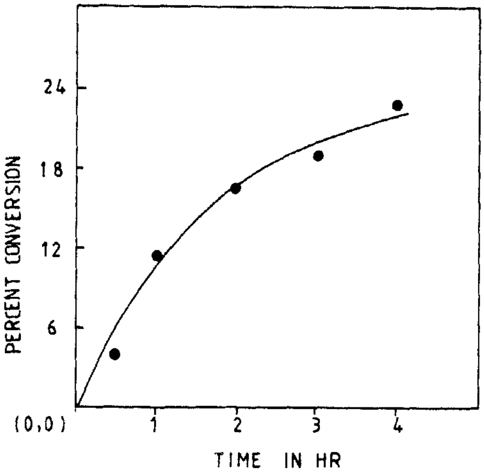

FIG. 2. Effect of reaction time on conversion using the [Co(acac)$_3$]-[Et$_3$Al] initiator system. Al/Co = 1.0, Co(acac)$_3$ = Et$_3$Al = 0.05 M, [ST] = [AN] = 4 M, 50°C.

In order to determine the most suitable Al/Co ratio for copolymerization, Al/Co ratio was varied from 0.5 to 4.0 by keeping the concentration of cobalt acetylacetonate constant and varying the concentration of triethylaluminum. It was observed that maximum conversions were obtained at an Al/Co mole ratio of 1.0 (Fig. 1). In our earlier study of copolymerization of acrylonitrile with vinyl acetate such a yield maximum was found at an Al/Co ratio of 2.0. As observed earlier, both above and below this ratio the conversion rapidly dropped. The results imply that a maximum number of active sites on catalyst is generated at an Al/Co ratio of 1.0. The behavior is indicative of a situation where acrylonitrile competes with both the active sites on catalyst and with triethylaluminum for complexation. The former leads to polymerization while the latter leads to an inactive monomer-Lewis acid complex. Increasing concentrations of triethylaluminum are expected to favor the latter situation.

The effect of reaction time on conversion at an Al/Co mole ratio of 1.0 is shown in Fig. 2. The conversion initially increases linearly with time and subsequently levels off. The effect of monomer and initiator concentration on the rate of polymerization (R_p) was studied at Al/Co = 1.0, 50°C, and 1 h reaction time. The results are shown in Figs. 3 and 4. It is observed that R_p shows an initial increase with both [M] and [I], reaches a maximum ([M] = 5, [I] = 0.05 M), and then decreases with a further increase in monomer and initiator concentrations. Such a variation of polymerization rate with changes

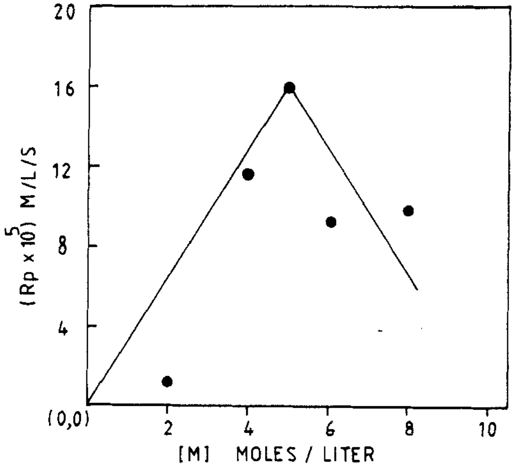

FIG. 3. Effect of monomer concentration on the copolymerization rate using the Co(acac)$_3$-Et$_3$Al initiator system. Al/Co = 1.0, [Co(acac)$_3$] = [Et$_3$Al] = 0.05 M, 50°C, 1 h.

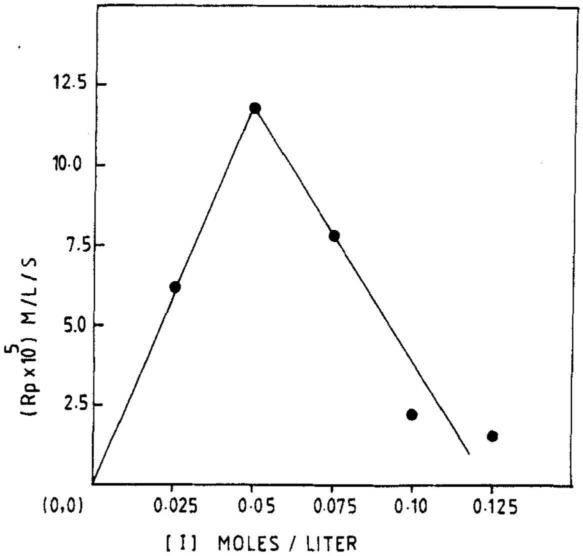

FIG. 4. Effect of initiator concentration on the copolymerization rate using the Co(acac)$_3$-Et$_3$Al initiator system. Al/Co = 1.0, [ST] = [AN] = 4 M, 50°C, 1 h.

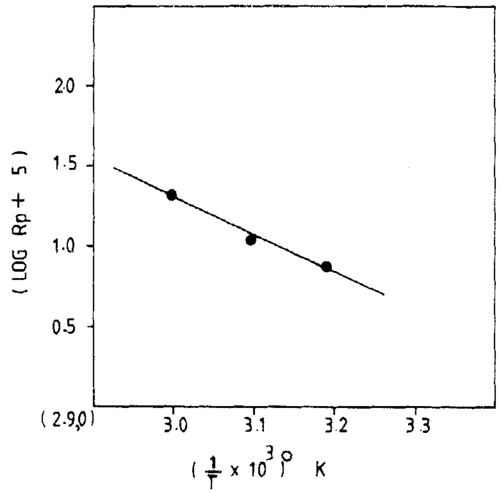

FIG. 5. Arrhenius plot of overall activation energy of copolymerization using the Co(acac)$_3$-Et$_3$Al initiator system. [Co(acac)$_3$] = [Et$_3$Al] = 0.05 M, [ST] = [AN] = 4 M, 1 h.

in the Al/Co ratio, monomer, and initiator concentrations has been observed before for polymerization of polar monomers with Ziegler-type catalysts [6].

It is well known that in Ziegler-type polymerizations the rate of polymerization is directly proportional to the number of active sites on the catalyst. In general, R_p also shows a linear dependence with monomer concentration. Consequently, the observation that the value of R_p decreases beyond a critical monomer concentration is indeed surprising. The reasons for this may lie in the fact that acrylonitrile is not only capable of $d\pi$-$p\pi$ complexing with the active sites on the catalyst, but also is a powerful n-electron donor. Beyond a critical monomer concentration, the active sites may be poisoned by interaction with the n-electrons of acrylonitrile which could lead to the observed drop in R_p. A similar hypothesis has been proposed to explain the role of Lewis bases or n-electron donors on Ziegler-Natta catalysts for olefin polymerizations [7].

The rate of polymerization was determined at three temperatures, i.e., 40, 50, and 60°C. The overall activation energy was calculated from the plot of log R_p vs 1/T and was found to be 10 kcal/mol (Fig. 5). This is in the range expected of coordination-type polymerizations and significantly below that of a free radical process.

The effect of feed composition on copolymer composition was

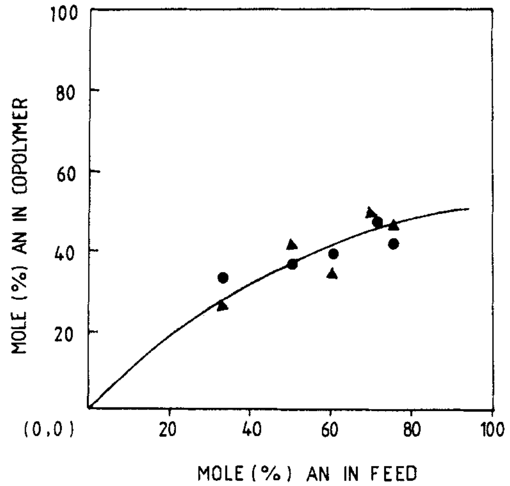

FIG. 6. Feed vs copolymer composition using the $Co(acac)_3$ - Et_3Al initiator system at 50°C in benzene and AIBN at 50°C in benzene. (●) Ziegler; (▲) AIBN.

TABLE 1. Effect of Hydroquinone on R_p and Viscosity[a]

Hydroquinone (mg)	$R_p \times 10^{-5}$ mol/L/s	η_{rel}[b]
-	11.7	1.298
68	5.2	1.220

[a] Conditions: [styrene] = [acrylonitrile] = 4 M; [$Co(acac)_3$] = [Et_3Al] = 0.05 M; molar ratio (Al/Co) = 1.0; 1 h; 50°C; molar ratio (initiator/HQ) = 2.0.

[b] 0.4% solution in DMF at 30°C.

determined over a range of 20 to 80 mol% of acrylonitrile in feed, using both the $Co(acac)_3$ -Et_3Al and the AIBN initiator system at 50°C. The results are shown in Fig. 6. Monomer reactivity ratios were evaluated graphically using a Fineman-Ross plot [8]. It was found that for the $Co(acac)_3$ -Et_3Al initiator system, r_1 (ACN) = 0.065 and r_2 (ST) = 0.400; for AIBN r_1 (ACN) = 0.027 and r_2 (ST) = 0.400. The latter values are in agreement with those reported in the literature [9].

The polymerization rate was susceptible to inhibition by added hydroquinone (Table 1). A similar observation was made by us earlier for the acrylonitrile-vinyl acetate system. Rate inhibition by hydroquinone has been used in the past to infer the presence of free radicals in the polymerization of acrylonitrile and methyl methacrylate using modified Ziegler-type catalysts [6, 10, 11]. Taken in conjunction with the fact that the monomer reactivity ratios of the $Co(acac)_2$ - Et_3Al initiator system are similar to that of AIBN, these results are indicative of a situation where both coordinate anionic and free radical sites are present on the catalyst.

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