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Lewis Acid - Complexed Tetramethylene Biradicals Can Initiate the Thermal Copolymerization of Indene with Acrylonitrile

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Summary

To clarify the mechanism of the spontaneous copolymerization of styrene with acrylonitrile, the corresponding reaction of its analog, indene, was investigated. The spontaneous free radical copolymerization of indene with acrylonitrile was promoted by Lewis acids. Spontaneous copolymerization rates comparable to those of styrene with acrylonitrile were found. For indene, the Mayo [$\pi^4 + \pi^2$] initiation mechanism, initially postulated for the spontaneous polymerization of styrene, cannot occur. Therefore the Flory mechanism, postulating a tetramethylene biradical initiating species, is proposed.

Introduction

Spontaneous Free Radical Copolymerization of St with AN - The spontaneous copolymerization of styrene (St) and acrylonitrile (AN) has been extensively studied by ourselves (1) as well as by other researchers (2). The bulk reaction is actually carried out thermally, i.e. without initiator, by several industrial companies. The polar difference between the two monomers makes these reactions faster than the thermal homopolymerization of styrene. In the case of styrene itself, two competing initiation mechanisms have been proposed, i.e. the Mayo (3) or the Flory (4) mechanisms. In the Mayo mechanism, an initial Diels-Alder reaction between the two molecules leads to a 1,2,3,8a-tetrahydronaphthalene derivative. This cycloaddition is followed by H-transfer from the doubly allylic hydrogen on the bridgehead position to another molecule to form two initiating monoradicals. Detection of the accompanying tetralin cycloadducts supports the Mayo mechanism for styrene. Camphorsulfonic acid retarded the polymerization by catalyzing the aromatization of this intermediate. In an earlier mechanism proposed by Flory (4) for styrene's spontaneous polymerization, the two molecules form a diradical tetramethylene intermediate by bond formation between the two β-carbons. This diradical can then either initiate free radical homopolymerization or close to a cyclobutane derivative. Isolation of a small amount of 1,2-diphenylcyclobutane supports the Flory mechanism for styrene to a minor competing extent.

The reaction of styrene with acrylonitrile was studied by Hasha, Priddy, Rudolf and Stark (2). They concluded that the Mayo mechanism did not operate here based on the structure of the trimers formed during the thermal polymerization, as well as the lack of effect of camphor sulfonic acid on the rate. They tentatively favored the polar Flory 1,4-biradical as the initiating species but did not detect 2-phenylcyclobutanecarbonitrile which would have supported this intermediate. Subsequently, Deshan Liu in this Laboratory did detect this cyclobutane among the small molecule adducts (1). Later Ferrando, Goffredi, Cantini and Bencini (5) were able to isolate and characterize the cyclobutane, so the Flory tetramethylene biradical is well established as one possible initiating intermediate in the styrene-acrylonitrile polymerization.

Lewis Acids Promote the Spontaneous Copolymerization of Styrene with Acrylonitrile - Lewis acids, added to a mixture of a donor hydrocarbon olefin and an acceptor olefin, complex to the lone pair electrons of the latter and increase the polarity difference between the two. Ester- and cyano-substituted olefins, such as acrylonitrile and methyl acrylate, are good acceptor olefin candidates leading to Lewis acid-base interactions. Complexation with the Lewis acid can make the polarity difference between the reacting olefins large enough to allow spontaneous initiation of free radical copolymerization (6,7). Spontaneous copolymerization of styrene with acrylonitrile complexed to zinc chloride occurs at temperatures as low as 40 °C.

Lewis Acid-Promoted of Spontaneous Copolymerization of Indene with Acrylonitrile - To shed further light on these initiation mechanisms, we shall investigate indene as a constrained planar analog of styrene. A remark about propagation is needed here. In the styrene experiments, high polymer was obtained in both spontaneous and initiated homo- and copolymerizations as expected. In contrast, free radical–initiated homopolymerization of indene gives only oligomeric products. Dostal and Raff (8) recognized that this is because chain transfer to allylic hydrogen competes with the desired propagation. This was confirmed by Breitenbach and Schindler (9,10). Accordingly one cannot study the spontaneous homopolymerization of indene to compare it to that of styrene.

However, strong polar effects can tilt this situation in favor of polymerization. Although not always recognized, a general rule can be stated: polarity differences between monomers favor propagation over allylic chain transfer. For example, propylene does not give high molecular weight copolymer with electron-poor acrylonitrile under free radical initiation, but more electron-rich isobutylene does so, even though it has twice as many allylic hydrogens. By complexing aluminum Lewis acids to acrylonitrile in order to enhance its electrophilic character, Hirooka (11) synthesized high molecular weight alternating copolymers with propylene or isobutylene. Logothetis (12) used boron trifluoride similarly, and Samoilov (13) surveyed propylene copolymerizations from this point of view.

Accordingly we can obtain high molecular weight copolymers of electron-rich indene with electron-poor acrylonitrile in presence of Lewis acids. The cycloadducts which occur during a Mayo mechanism cannot form for indene: a $\pi^4 + \pi^2$ cycloadduct would be impossibly strained. Cyclobutane formation is unfortunately also excluded because of difficulty in fusing a 4-ring to a 5-ring; for example, maleic anhydride, despite its high electrophilicity, does not undergo thermal $\pi^2 + \pi^2$ cycloaddition with electron-rich olefins. Therefore we cannot expect cyclobutane products which could support a biradical mechanism. However, since the Mayo mechanism cannot operate, any observed spontaneous copolymerization will be interpreted as initiation by a Lewis acid-complexed Flory polar tetramethylene biradical. The criteria used in our earlier mechanistic studies (1,7,14-16) will apply except for the absence of the cyclobutane small molecule.

Only very limited information on the copolymerization of indene with acrylonitrile was available in the literature. Mikhael (17) obtained copolymers of indene with acrylonitrile using free radical initiation, while Nagai (18) found a spontaneous copolymerization of indene with acrylonitrile complexed to $ZnCl_2$. This catalyst will be examined more closely in the present work.

Recently we also used lithium perchlorate as a Lewis acid in alternating vinyl copolymerizations (19,20). This Lewis acid had been widely used in organic chemistry but not in polymer chemistry. We also investigated its use in the indene/acrylonitrile copolymerization.

Experimental

Materials and Instrumentation - Indene ID (98%) and acrylonitrile AN (99%) were purchased from Aldrich. After passing through a column of aluminum oxide, indene was distilled over CaH_2 under reduced pressure and stored at < 5 °C. Acrylonitrile was distilled over CaH_2 under reduced pressure and stored at < 5 °C. Azobisisobutyronitrile AIBN was recrystallized from methanol. $LiClO_4$ and $ZnCl_2$ were dried under reduced pressure at 90 °C. Solvents acetonitrile (MeCN), propionitrile (PN), γ-butyrolactone, sulfolane were dried over CaH_2 and distilled under reduced pressure.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Gemini-200 spectrometer at 200 MHz. IR spectra were recorded on a Nicolet Impact 410 Fourier Transform infrared spectrometer (FTIR). Gel permeation chromatography (GPC) was obtained using THF as eluent, an ultraviolet detector at 254 nm and a set of Phenomenex® columns (10^3-10^5) calibrated versus polystyrene standards. Elemental analyses were performed by Desert Analytics, Tucson. AZ.

Polymerization Procedure - To a flame-dried polymerization tube, the calculated amount of AN and Lewis acid (if necessary) and solvent (if necessary) were added, the mixture was stirred vigorously at room temperature to achieve complete dissolution. ID was added and the mixture stirred again at room temperature. The clear homogeneous reaction mixture was degassed by three freeze-thaw cycles and kept in the dark to avoid any photo-initiation, under nitrogen with stirring at the given temperature for the reaction time. Using this procedure and this order of addition, the homopolymerization of either monomer was avoided. At the end of reaction time, the clear viscous mixture was diluted with acetone and poured into excess ether. The precipitated copolymer was filtered, and washed with ether and dried at 60 °C under reduced pressure. The copolymer was redissolved in acetone and precipitated into excess ether, and the solid was separated by filtration, and washed with ether, and dried under reduced pressure until constant weight. The obtained copolymers were characterized by FTIR, ^{1}H-NMR, GPC, and elemental analysis. IR (KBr) 3050-3150 cm^{-1} (aromatic C-H str.); 2900-3000 cm^{-1} (aliphatic C-H str.); 2238 cm^{-1} (CN str.). ^{1}H-NMR (DMSO-d_6) δ 7.2 (4H, aromatic); 3.2 (1H, CH from AN); 2.5 and 2.8 (2H, CH from ID); 2.0 (4H, 2 CH_2 from ID and AN). The filtrates were collected and extracted with excess ether. The ether layer was investigated for small molecules. As expected, negligible material was found.

Results

Initiated Copolymerizations of ID/AN - The copolymerization of indene and acrylonitrile was investigated in numerous conditions, summarized in Table 1. All polymerizations were carried out at 75 °C unless otherwise specified. In a control experiment to demonstrate the feasibility of deliberate free radical–initiated copropagation, AIBN-initiated copolymerizations using a 50/50 monomer feed ratio led to moderate yields of copolymer, but the average MW was only 8,000. Accordingly chain transfer is still present, though much less than in indene homopolymerization.

Table 1: The Copolymerization of Indene and Acrylonitrile at 75 °C

mol% AN in feed	Lewis Acid/ Additive (AN equiv.)	Solvent[c]	Time (h)	Polymer Yield (%)	SEC MW(PDI)	mol% AN in copol.[b]
50	AIBN		24	30	8,000 (1.3)	
50	AIBN	MeCN	24	54		
50		None	24	Trace		
66		None	24	7		71
75		None	24	14	9,200 (1.6)	60
80		None	24	19	18,000 (1.8)	68
84		None	24	26		69
87		None	24	30		73
66		MeCN	24	Trace		
75		MeCN	24	8		53
84	$ZnCl_2$, 0.5		20	48.0	120,000 (5.0)	60
84	$ZnCl_2$, 1.0		20	68	200,000 (7.0)	60
50	$ZnCl_2$, 1.0	γ-Butyrolactone	20	20.5	65,000 (3.0)	70
50	$ZnCl_2$, 1.0	Sulfolane	20	54.5	146,000 (4.6)	52
66	$LiClO_4$, 1.0	None	17	36.7	45,000 (2.1)	49
80	$LiClO_4$, 1.0	None	17	40.6	43,000 (2.4)	68
84	$LiClO_4$, 1.0	None	17	51.7	42,000 (2.0)	66
87	$LiClO_4$, 1.0	None	17	79.5	30,000 (1.9)	73
89	$LiClO_4$, 1.0	None	17	77.4	24,000 (1.6)	
66	$LiClO_4$, 1.0	MeCN	24	9.6	25,000 (3.1)	58
66	$LiClO_4$, 1.0	PN	24	7.7	20,000 (2.2)	58
66	$LiClO_4$, 1.0	γ-Butyrolactone	20	18.7	23,000 (2.3)	63
66	$LiClO_4$, 1.0	Sulfolane	24	28.5	25,000 (2.3)	61

a. Added solvents 2.7M, PN = propionitrile
b. Elemental Analysis, NMR Composition

Spontaneous Copolymerizations of ID/AN - Neither indene nor acrylonitrile, when heated up by themselves without any Lewis acids, undergoes spontaneous homopolymerization. Spontaneous copolymerizations between them do occur, although slowly, at 75 °C, only a trace of polymer being obtained after 24 h at a 1/1 monomer feed ratio. We investigated the influence of the monomer feed ratio on these polymerizations in bulk. The yields rose steadily as the AN concentration increased. Using 87 % AN in the monomer feed, the yield obtained was 30 %. The copolymers consistently contained about 70 % of acrylonitrile units because excess AN was present. In acetonitrile solution, the spontaneous copolymerizations are even slower.

Spontaneous Copolymerizations of ID/AN/ZnCl$_2$ - The addition of zinc chloride increased the copolymer, yields, and molecular weights. In bulk, 0.5 equivalent ZnCl$_2$ relative to AN gave 48% and 1 equivalent gave 68% yields, in 20 hours. The molecular weights were much higher, up to 200,000. The molecular weight distributions were very broad, between 3 and 7. The AN content in the copolymers increased with AN content in the feed. The polar non-complexing solvent sulfolane gave slightly lower yield and lower molecular weights, nearly alternating in composition. Both γ-butyrolactone and propionitrile as solvent gave only 21 % and 2 % polymer, respectively, probably because they are donor solvents and competed with AN for ZnCl$_2$.

Spontaneous Copolymerization of ID/AN/LiClO$_4$ - Lithium perchlorate added to the copolymerization as a Lewis acid in bulk conditions also led to much higher yields than without Lewis acid present. When the feed contained 87 % AN, yields of up to 80 % were obtained after 17 hours. Again excess AN led to ~70 %AN in the copolymers. Lower average molecular weights but much narrower molecular weight distributions were observed than for zinc chloride. Here, polymerization in γ-butyrolactone or sulfolane succeeded, but acetonitrile and propionitrile as solvents gave lower yields because they competed with AN for complexation to LiClO$_4$.

Discussion

Spontaneous Copolymerization of ID/AN - Under the conditions we studied, neither indene nor acrylonitrile by themselves homopolymerizes. ID and AN do copolymerize slowly. Those copolymers contained approximately 70 mol% of AN. The conversion increased with increasing AN/ID ratio. This is ascribed to an increase in the initiation rate; higher AN concentrations favor the formation of the tetramethylene diradical intermediate as it does for styrene (1). The copolymerization is initiated through a reaction of an indene molecule with an acrylonitrile molecule to form a biradical tetramethylene, as shown in Scheme 1, consistent with a Flory mechanism for ID/AN.

Spontaneous Copolymerization of ID/AN/ZnCl - Addition of ZnCl$_2$ to the monomer mixture led to higher rates, higher conversions, and higher molecular weight. The Lewis acid complexes with AN to make it more electrophilic, resulting in a larger polarity difference between the two monomers. This enhances the rate of initiation, which results in higher yields. The polarity difference also reduces the apparent occurrence of chain transfer leading to higher molecular weights, the increased polarity difference also leads to more alternation in the propagating step. The increased polarity difference between the monomers also leads to enhanced rates for cross propagation reaction, as previously demonstrated by Mikhael (21) and Bamford (22). The copolymers contained 60% AN, closer to alternating even using a feed ratio ID/AN of 13/87. Broad molecular weight distributions are observed. This is in agreement with earlier observations when using this Lewis acid. Speculatively, ZnCl$_2$ has two open coordination sites, leading to a mixture of complexes, AN/ZnCl$_2$ and (AN)$_2$/ZnCl$_2$, which give competing propagating species and broad MWD's. Much lower yields are obtained if the copolymerizations are performed in solution, in agreement with the idea that the initiation involves a bimolecular reaction. In this

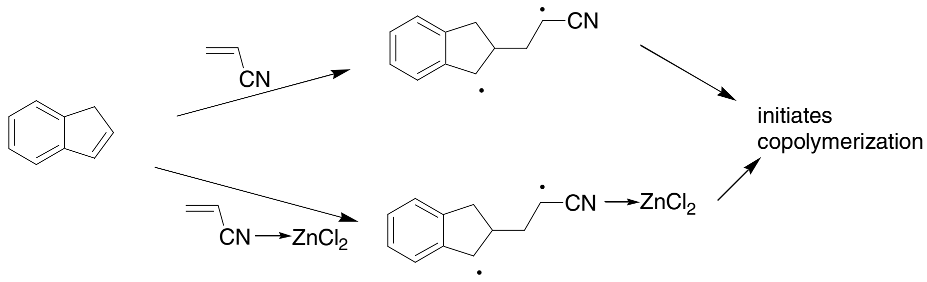

Figure 1: Proposed Initiation Mechanisms with or without Lewis Acid

case we postulate that the same tetramethylene biradical intermediate is now complexed with zinc chloride.

Spontaneous Copolymerization of ID/AN/LiClO$_4$ - Addition of LiClO$_4$ has a very similar effect on the spontaneous ID/AN copolymerization as addition of ZnCl$_2$. The yields are in the same range as with ZnCl$_2$. The molecular weights are still high, although lower than with ZnCl$_2$. LiClO$_4$ has only one coordination site, leading to a more uniform complexed monomer for the copolymerization; the molecular weight distributions are ~2, which is reasonable for a classical free radical polymerization. For a 25/75 ID/AN ratio with one equivalent of Lewis acid, a 50/50 copolymer composition is obtained, indicating the formation of an alternating copolymer and a large polarity difference between the polymerizing monomers.

Again much lower yields are obtained if the copolymerizations are run in solution, in agreement with the idea that the initiation involves a bimolecular reaction. Donor solvents also compete for LiClO$_4$. In this case we postulate that the common tetramethylene biradical is complexed with Li$^+$.

Conclusions

The rate of thermal copolymerization of ID with AN in the absence of ZnCl$_2$ is rather similar to the spontaneous copolymerization of styrene and AN. ID is a β-substituted styrene, resulting in a slower rate. However its flat structure stereoelectronically enhances radical stabilization, so the two effects roughly offset each other.

In the presence of a Lewis acid, distinctions appear between styrene and indene. The rate of St/AN copolymerization is strongly enhanced by ZnCl$_2$, while the copolymerization rate of ID/AN is enhanced to a lesser extent. This could be due to geometric constraints with indene. The main difference between styrene and indene is the ability of styrene to undergo an electrocyclic reaction to form a Mayo intermediate which readily forms two monoradicals.

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