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Effect of $ZnCl_2$ on the Spontaneous Copolymerization of Acrylonitrile with Substituted 1,3-Dienes

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ABSTRACT: Acrylonitrile was allowed to react with three substituted hydrocarbon 1,3-dienes, namely, 2,3-dimethyl-1,3-butadiene (DMB), 4-methyl-1,3-pentadiene (MPD), and isoprene (IP) in 1,2-dichloroethane in the presence of various amounts of zinc chloride at different temperatures. Alternating copolymers and [4 + 2] cycloadducts formed spontaneously. The structure of the diene and its electron-rich character control the product distribution. In the reaction of DMB and AN, raising the temperature and increasing the $ZnCl_2$ concentration enhance the cycloaddition process, while the maximum yield of the copolymerization is at 45 °C. At higher temperatures, no copolymers formed. With MPD, only copolymer is formed because the two terminal methyl groups preclude the concerted [4 + 2] cycloaddition. IP is less reactive than DMB, and the overall yields are lower. These results are in agreement with a postulated mechanism involving competition between a π-allyl 2-hexene-1,6-diradical and concerted cycloaddition. A H-transfer mechanism is suggested to explain the lack of copolymer for DMB/AN or IP/AN at higher temperatures and $ZnCl_2$ concentrations.

Introduction

We have extensively studied the competition between the spontaneous polymerization and the [2 + 2] cycloaddition which occur upon mixing an electron-rich olefin with an electron-poor olefin.[1-4] The key species for both the observed polymerization and the [2 + 2] cycloaddition was postulated to be a tetramethylene intermediate, formed by bond formation between the two olefins.

More recently these studies were extended to the reactions of electron-rich 1,3-dienes with electron-poor olefins.[5-7] In many cases, alternating copolymers were obtained spontaneously alongside the expected [4 + 2] cycloadducts. In analogy to the olefin–olefin reactions, we proposed bond formation between the s-trans diene and electrophilic olefin to form a π-allyl 2-hexene-1,6-diradical intermediate, which is postulated to be the initiating species for the observed free-radical copolymerizations. The [4 + 2] cycloadducts arise from a competing concerted electrocyclic reaction from the s-cis conformation of the diene.

Bond formation, and therefore spontaneous copolymerization, between the two comonomers can only take place if there is a substantial polarity difference between the two reaction partners. For example, acrylonitrile (AN), which is a weak acceptor olefin, requires heating to cause spontaneous copolymerization with or cycloaddition to hydrocarbon dienes, such as 2,3-dimethyl-1,3-butadiene[5] or 4-methyl-1,3-pentadiene.[7] However, spontaneous copolymerization at room temperature occurs readily if the polarity difference between the comonomers is sufficiently large, for example, for the monomer pair 1-methoxy-1,3-butadiene and fumaronitrile.[1,6] Very large electronic disparity favors cycloaddition over copolymerization, as observed in the case of mixing 1-methoxy-1,3-butadiene with methyl β,β-dicyanoacrylate.[6]

Lewis acids increase the electrophilicity of the electron-poor olefin by complexing to its lone pair electrons, thereby increasing the electron disparity between the reaction partners. Lewis acid complexation thus facilitates [4 + 2] cycloadditions;[8] for example, $ZnCl_2$ promotes several Diels–Alder cycloadditions[9] and $AlCl_3$ is reported to catalyze the Diels–Alder reaction of isoprene and AN.[10] Lewis acid complexation also results in alternating copolymerization for many monomer pairs, which leads to random copolymers in its absence. Finally, Lewis acid complexation can also lead to initiation of the spontaneous polymerization for moderately electron-rich and electron-poor monomer pairs.[11]

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In this paper we report the effect of a typical Lewis acid, $ZnCl_2$, on the reaction of AN with three substituted-hydrocarbon 1,3-dienes, namely, 2,3-dimethyl-1,3-butadiene (DMB), 4-methyl-1,3-pentadiene (MPD), and isoprene (IP). Our attention will be confined to $ZnCl_2$, for which substantial literature is available (see below). Also, we shall concentrate our attention on the competition between the cycloadditions and the spontaneous initiation of the alternating copolymerizations rather than on the alternating propagation reaction, which has been studied and reviewed extensively.[11]

Background

Furukawa and his colleagues examined the competition between cycloaddition and spontaneous copolymerization for the reaction of 1,3-butadiene (BD) with AN in the presence of $ZnCl_2$.[12] Both reactions were reproducibly accelerated with increasing concentration of $ZnCl_2$ and with temperature (up to 60 °C). No induction period was observed. UV light accelerated the polymerization but did not affect the cycloaddition. No viscosities were reported, and the copolymers may have been cross-linked. These workers concluded that the two products arose from different energy states of a common intermediate.

Further examination of this reaction was done by Kuran and his colleagues.[13] At 50 °C an induction period was noted, after which copolymer yield increased with time, leveling off at 22%. Very low copolymer yields were obtained at both higher and lower temperatures. No viscosities were reported, which again suggests that these copolymers may have been cross-linked.

Cyclic 1,3-dienes have also been investigated. An extensive systematic study was reported in several contributions by Nagai and his colleagues.[14-17] Reaction of cyclopentadiene and AN/$ZnCl_2$ only results in cycloaddition, while 1,3-cyclohexadiene with AN and $ZnCl_2$ gave both copolymer and cycloadduct.[17] The proportion of copolymer was much greater when 1,3-cycloheptadiene was used.[14] Again, smoothly reproducible copolymerization and cycloaddition took place. No induction period was noted up to 70 °C, and these copolymers were soluble. The copolymerization rates were 1.5 order in each component, whereas the cycloaddition was first order in each. 1,3-Cyclooctadiene again gave both copolymer and cycloadduct.[16] Nagai proposed that the ratio of copolymer to cycloadduct is related to the dihedral angle between the double bonds in the 1,3-cyclodienes.

Results

The reactions of AN with the investigated 1,3-dienes DMB, MPD, and IP were carried out in 1,2-dichloroethane (DCE) solutions (3 mol/L) at different temperatures (25−100 °C) in the presence of various amounts of $ZnCl_2$ (O−50 mol % based on AN). All polymerizations were run in the absence of light. The polymerization mixture was added to methanol, and the precipitated polymer was collected. The filtrate was concentrated at reduced pressure. The residue was extracted with ether and water, the ether layer was dried, the solvent was evaporated, and the remaining liquid cycloadduct was analyzed by ^1H NMR.

Reference experiments were carried out for each diene. A free-radical inhibitor, 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (3 mol %) was added or AN was replaced by its nonpolymerizable equivalent propionitrile. Neither experiment produced any polymeric material for any diene after 24 h at 50 °C. These blank experiments prove several things: the copolymerization is free radical, and the diene does not undergo cationic homopolymerization in the presence of $ZnCl_2$ under the used reaction conditions. For the DMB/AN system, the formed cycloadduct and the formed copolymer were added to fresh reaction mixtures, but they did not affect the results.

Table 1. Reactions between AN and DMB[a] in 1,2-Dichloroethane

temp (°C)	$ZnCl_2$ (mol % vs AN)	time (h)	cycloadduct (% yield)	copolymer (% yield)	M_w (SEC)
25	0	24	2.6	0	
	10	8	3.9	0	
	10	24	6.5	0	
	30	24	34.1	0	
	50	24	56.1	0	
45	0	24	2.8	0	
	10	8	22.7	2.4	
	10	24	34.2	13.0	1.33×10^5
	30	24	57.5	7.0	
	50	24	62.5	5.0	
65	0	24	2.5	11.2	1.31×10^5
	10	8	28.8	trace	
	10	24	39.9	3.4	
	30	24	62.0	1.0	
	50	24	68.8	0	
85	0	24	25.4	22.4	1.31×10^5
	10	24	47.0	1.0	
	30	24	70.2	0	
	50	24	74.9	0	
100	0	24	40.0	38.0	
	10	24	50.9	0	
	30	24	75.8	0	
	50	24	80.9	0	
25/UV/BME[b]	10	5 min		98.2	cross-linked
60/AIBN[c]	10	5 min		99.6	cross-linked

[a] Each 3 mol/L. [b] Benzoin methyl ether (BME) 1 mol % based on AN at 25 °C with UV light. [c] Azobisisobutyronitrile (AIBN) 1 mol % based on AN at 60 °C.

DMB/AN Reaction (Table 1). In the absence of $ZnCl_2$, very little cycloaddition occurs between DMB and AN at temperatures below 60 °C, while at higher temperatures (85 and 100 °C), the Diels−Alder cycloadduct was produced. These results confirm earlier results from this laboratory.[5] As expected, in the presence of 10−50 mol % $ZnCl_2$ based on AN, the yield of cycloadduct increased dramatically. Also, raising the reaction temperature from 25 to 100 °C, at a constant concentration of $ZnCl_2$, increased the yield of cycloadduct.

The data in Table 1 also show that, in absence of $ZnCl_2$, no copolymer formed after 24 h at temperatures below 65 °C. At 85 and 100 °C (24 h), the copolymer yield increased to 22 and 38%, respectively, again in agreement with earlier work.[5] In the presence of $ZnCl_2$, again no copolymer formed at room temperature. At 45 °C and 10 mol % $ZnCl_2$, copolymer formed in 13% yield after 24 h. Compared to the competing cycloaddition, copolymerization is a very slow reaction. Remarkably, the yield of copolymer at 45 °C *decreased* to 7 and 5% when increasing the $ZnCl_2$ concentration was to 30 and 50 mol %, respectively. Raising the temperature to 65 °C further decreased the copolymer yield, and at 100 °C, no copolymer formed in the presence of $ZnCl_2$.

The dependence of cycloadduct and copolymer yields on the reaction time at 45 °C in the presence of 10 mol % $ZnCl_2$ is shown in Figure 1 for the AN/DMB and AN/IP systems. The cycloadduct yields follow reasonably smooth curves, showing the reproducibility of the data.

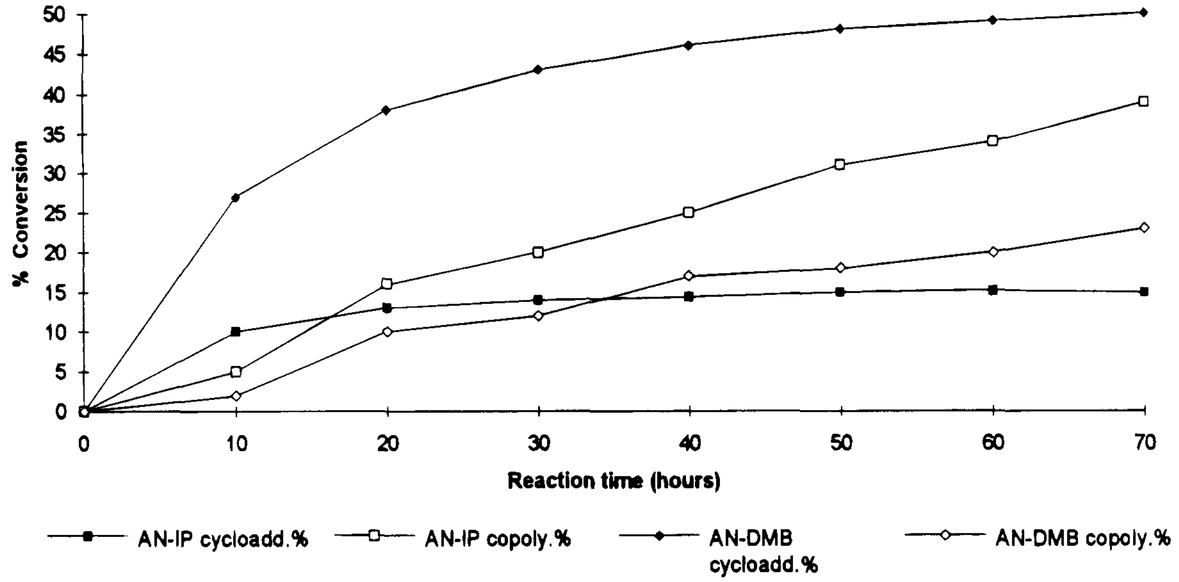


Figure 1. Relation between time and percent conversion for AN/IP and AN/DMB systems in the presence of 10 mol % $ZnCl_2$ at 45 °C in 3 mol/L DCE solutions.

Table 2. Reactions between AN and MPD in 1,2-Dichloroethane[a]

temp (°C)	$ZnCl_2$ (mol % vs AN)	time (h)	copolymer[b] (% yield)
25	0	2.4	trace
	5	0.5	8
	5	2	21
	10	0.5	38
	10	2	59
65	0	24	19
	10	0.5	47
	10	2	69

[a] Each 3 mol/L. [b] No cycloadduct detected in the product of this sytem. [c] All the obtained copolymers are insoluble and crosslinked.

The copolymer yield curves (Figure 1) show a very slow reaction in the first stages. The reaction mixtures were homogeneous and stirrable in all cases, becoming more viscous as the polymerization proceeded. As shown in Table 1, two reference experiments were done in the presence of 10 mol % $ZnCl_2$ with deliberately added free-radical initiators. In both cases, almost 100% conversion to cross-linked copolymer was observed after only 5 min.

^1H NMR spectroscopy and elemental analysis are both in agreement with our previous work.[5] These analyses confirm the proposed alternating structure of the copolymers ($M_w = 1.3 \times 10^5$). These isolated copolymers were soluble.

MPD/AN Reaction (Table 2). On the basis of its degree of substitution, we can assume that MPD is about as electron-rich as DMB. However, its two methyl groups at one terminal carbon atom hinder [4 + 2] cycloaddition.[7,18] MPD reacted with AN in the presence of 10 mol % $ZnCl_2$ at 25 and 65 °C to produce insoluble copolymers is 60 and 70% yield, respectively, in only 2 h. The copolymerization in this case is much faster than for DMB (or for IP; see below), while no cycloadduct is formed. These copolymers were insoluble, and presumably cross-linked, even at low conversions.

IP/AN Reaction (Table 3). Isoprene is a less electron-rich diene than either DMB or MPD. The tendency toward cycloaddition was pronouncedly less than for DMB. The yields are lower over the whole temperature range examined at different $ZnCl_2$ concentrations.

Table 3. Reactions between AN and IP[a] **in 1,2-Dichloroethane**

temp (°C)	$ZnCl_2$ (mol % vs AN)	time (h)	cycloadduct (% yield)	copolymer[b] (% yield)
25	0	24	0	0
	10	8	2.7	0
	10	24	5.9	0
	30	24	9.5	0
45	0	24	2.2	0
	10	8	8.8	5.9
	10	24	13.6	28.3
	30	24	21.0	34.2
65	0	24	3.1	3.3
	10	8	14.2	6.7
	10	24	23.1	29.0
	30	24	31.5	24.5
85	0	24	12.5	22.0
	10	24	26.9	14.1
	30	24	35.8	3.1

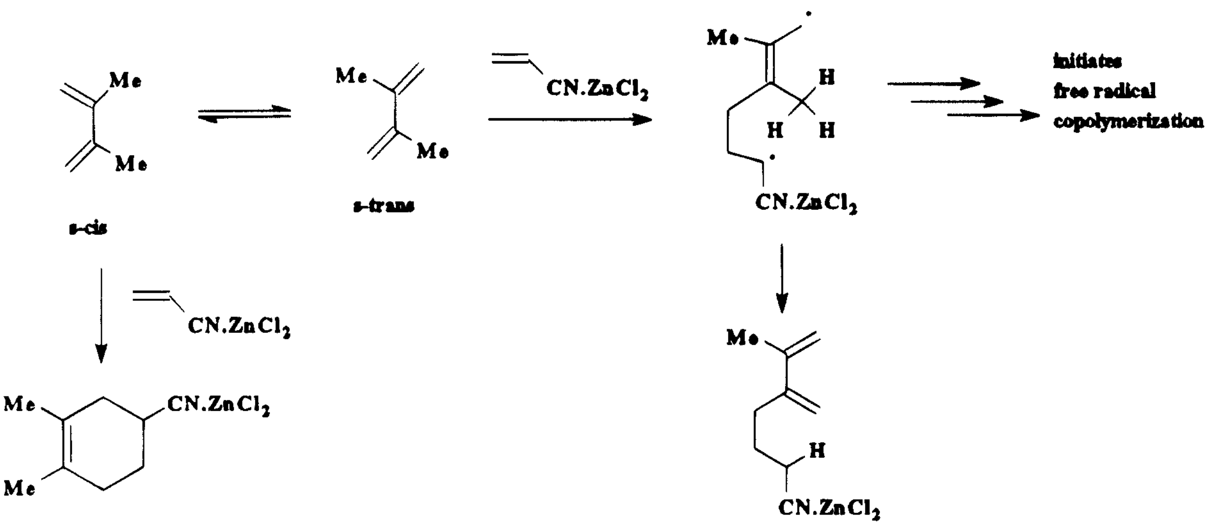
[a] Each 3 mol/L. [b] All the obtained copolymers are insoluble cross-linked materials.

Similarly, due to the fact that IP is a weaker donor diene than DMB, higher temperatures are required to obtain any copolymer of IP and AN. However, in the presence of $ZnCl_2$, higher copolymer yields are observed for IP than for DMB. At 45 °C and 10 mol % $ZnCl_2$, a 28% yield of copolymer was isolated after 24 h, compared to 13% for DMB/AN. The amount of IP/AN copolymer increased to 34% when 30 mol % $ZnCl_2$ used. Raising the temperature from 65 to 85 °C and increasing the $ZnCl_2$ concentration again favored the cycloaddition and disfavored the copolymerization, whose yield actually *decreased* at 85 °C and 30 mol % $ZnCl_2$ to only 3%. Figure 1 shows that for IP, as for DMB, the yield of cycloadduct increases normally with time but that of copolymer shows a slow first stage and then increases. IR and elemental analyses showed that the formed polymers are 1:1 copolymers. Their insolubility attested to cross-linking.

Discussion

The spontaneous copolymerizations and [4 + 2] cycloadditions of acrylonitrile with three hydrocarbon dienes of varying electron density and steric hindrance have been studied at several temperatures with varying amounts of $ZnCl_2$.

Scheme 1. Proposed Mechamism for DMB and AN in the Presence of ZnCl$_2$



The formation of a [4 + 2] cycloadduct from DMB/AN and IP/AN behaved normally in every way. It was faster for the more electron-rich DMB than for IP. Comparing our results to the data reported by Kuran,[13] both DMB and IP underwent the [4 + 2] cycloaddition with AN/ZnCl$_2$ faster than the parent 1,3−butadiene, again in agreement with the more electron-rich character of DMB and IP compared to butadiene. The rates proceeded normally and reproducibly with time. They were accelerated monotonically by ZnCl$_2$ and by increased temperature. These results are in complete accord with the organic chemistry literature on acceleration of Diels−Alder reactions by Lewis acids.[8−10] No cycloaddition was observed for MPD because of steric hindrance.

Just as for the reactions of 1,3-dienes with acrylonitrile alone,[5] the ZnCl$_2$-promoted spontaneous reactions with AN gave reproducible yields of copolymers, showing that these copolymers are not due to impurities. The electron-rich MPD rapidly gave substantial yields of copolymer. Increasing the ZnCl$_2$ concentration and/or reaction temperature raised the amount of copolymer formed. Less electron-rich IP reacted more slowly to give modest yields of copolymer. For both MPD and IP, the latter only at lower temperature, the rates greatly increase upon ZnCl$_2$ addition. This is attributed to the greater polarity difference between the reactants. DMB gave anomalously low yields of copolymer at higher temperatures and higher ZnCl$_2$ concentrations.

As we have previously postulated for the uncatalyzed case, the competition between cycloaddition and spontaneous copolymerization is governed by the s-trans/s-cis equilibrium, as shown in Scheme 1. The s-cis form undergoes Woodward−Hofmann allowed concerted [4 + 2] cycloaddition. The s-trans form undergoes bond formation with ZnCl$_2$-complexed AN to form a 2-hexene-1,6,-diradical−ZnCl$_2$ complex. This then initiates free-radical copolymerization. The rates of both reactions are enhanced by the electron-rich diene character and by the increased electrophilic character of AN coordinated to ZnCl$_2$. The effect of the ZnCl$_2$ complexation might be greater for cycloaddition than for initiation of copolymerization.

The yields of copolymer from DMB and AN/ZnCl$_2$ at higher temperatures and higher ZnCl$_2$ concentrations are anomalously low. Because copolymer is formed without ZnCl$_2$, or with ZnCl$_2$ at the lower temperatures, we know that at least a small amount of free radicals are formed in the system. Very few radicals were formed spontaneously, as witnessed by the very low copolymer yield and the high molecular weights. Reference experiments show that this copolymerization proceeded very fast if free radicals were introduced in the system by addition of a free-radical initiator. Therefore, we conclude that the few radicals formed in the DMB/AN mixture in the presence of ZnCl$_2$ are being destroyed. We postulate a H-atom transfer from the nearby methyl group to the complexed AN radical end forms a new diene, as shown in Scheme 1. This process would consume the diradical. The new diene, formed in only very low quantity, escapes detection by taking part in the cycloaddition or copolymerization. This reaction would more readily occur for the ZnCl$_2$-catalyzed DMB/AN reaction than for the uncatalyzed case because of the greater polarity difference between the components in the former. Moreover, it shows the steepest dependence on temperature (largest activation energy). This novel reaction must sweep out diradicals very efficiently, in view of the total lack of copolymerization at higher temperatures.

For IP, the same phenomenon, namely, decreased copolymer yield at higher temperatures and at higher ZnCl$_2$ concentrations, is also observed, but not as dramatically as for DMB. In IP, two possible 2-hexene-1,6-diradicals can form, namely, with the methyl group in the 2- or in the 3-position. Only the latter would lead to the postulated H-transfer to the AN radical end. Also, the polarity difference between the two radical ends in the 2-hexene-1,6-diradical intermediate is less pronounced.

The copolymers of IP and MPD are cross-linked. The lack of cross-linking for the DMB copolymers may be due to the tetrasubstituted nature of the double bonds in these copolymers. Nevertheless, Nagai's copolymers of cyclic 1,3-dienes also remained soluble and formed in good yield.[16,17]

Experimental Section

Instrumentation. This was described in a previous paper.[6]

Solvents and Reactants. 1,1-Dichloroethane was dried over CaH$_2$ and distilled before use. Acrylonitrile, isoprene, and 2,3-dimethyl-1,3-butadiene (Aldrich) were distilled just before use. 4-Methyl-1,3-pentadiene was separated from its mixture with *trans*-2-methyl-1,3-pentadiene (75%, Aldrich) according to Bachman.[19] ZnCl$_2$ (Aldrich) was dried under vacuum at 300 °C.

Typical Reaction Procedure. Zinc chloride in a flame-dried polymerization tube was heated at 300 °C for 15 min under vacuum. The calculated amount of acrylonitrile was added, and the mixture was stirred vigorously under argon. Solvent and electron-rich diene were added. The reaction mixture was degassed by the freeze–thaw procedure and kept under argon with stirring at the given temperature and time. At the end of the reaction time, the tube was cooled in ice and the mixture poured over excess of methanol-containing HCl and a small amount of free-radical inhibitor. The precipitated polymeric materials were filtered, washed with warm methanol, and dried under vacuum at 50 °C to constant weight. The obtained polymers were analyzed by IR, NMR, SEC, and elemental analysis. The filtrate was concentrated at room temperature using a rotary evaporator and extracted with ether/water. The ether layer was dried over anhydrous $MgSO_4$ and evaporated. The dry residue was distilled under vacuum and characterized by ^1H NMR. Spectroscopic and analytical details of all the cycloadducts and copolymers formed can be found in previous papers.[5-7]

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