Copolymerization of Acrylonitrile and 1-Hexene in the Presence of Lewis Acids

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ABSTRACT: Several boron Lewis acids have been used to effect the copolymerization of acrylonitrile and 1-hexene in methylene chloride and benzene solution. In all cases 1:1 copolymers have been prepared provided the Lewis acid is strong enough to complex the nitrile. The effect of substituents in the α position of acrylonitrile has also been examined and the structure of these polymers is discussed. Ultraviolet spectroscopy and solution calorimetry have been used to study the reaction mechanism of these polymerizations. No physical evidence for charge-transfer intermediates has been found, and the reaction mechanism is discussed in view of these results.

The first report[1] of the copolymerization of two monomers in the presence of a Lewis acid was made several years ago. At that time it was found that complexing acrylonitrile with aluminum chloride or tin tetrachloride caused a change in the relative reactivities of acrylonitrile and methyl methacrylate. However, it was only recently recognized[2] that complexing polar monomers with Lewis acids generally caused wide variation in relative reactivities of monomers. In these first examples, polymer compositions varied with monomer feed ratios, but it was not long before 1:1 copolymers were prepared under similar reaction conditions.

Leading work by Hirooka,[3] in which 1:1 copolymers of acrylonitrile and α olefins were prepared in the presence of aluminum Lewis acids, appeared to spark numerous research efforts in this area. This is understandable, since changes in solvent or other reaction conditions usually have little effect on monomer reactivity ratios. The fact that 1:1 copolymers are always prepared with a variety of monomer combinations has led to a number of recent papers[4-6] which propose that the unusual selectivity is a result of the formation of a molecular complex between the two monomers. It is thought that the Lewis acid complex of the polar monomer increases its electron-accepting ability to the point that molecular complexes are formed between the polar monomer–Lewis acid complex and the α olefin. The molecular complex can then act as a unit and polymerize to yield 1:1 alternating copolymers. Initiation by free-radical sources,[3] ultraviolet radiation,[7] or spontaneous mechanisms[4,8] have been reported in these systems. Although claims of molecular complexes as reaction intermediates are frequent, physical studies to prove their existence in polymerization media are rare and usually not well documented. There is some evidence,[9] however, to suggest that there is interaction between the acrylonitrile–zinc chloride complex and benzene.

It is of interest to note that the idea of a molecular complex as an intermediate in polymerization reactions is not new and was first suggested by Bartlett[10] to explain the "alternating tendency" he observed in allyl acetate–maleic anhydride copolymerizations. Walling,[11] however, preferred to view the interaction leading to alternating copolymers of maleic anhydride and substituted styrenes as a transition-state phenomenon. He postulated that the electron-donating or -accepting properties of the monomer were important during interactions of the growing polymer radical. The selectivity leading to alternation was then based upon reaction of the polymer radical with the monomer which would give the most stable transition state.

The copolymerization of maleic anhydride with several comonomers has been studied recently by a number of workers[12-14] and bears remarkable similarity to examples of copolymerization with Lewis acid complexes of polar monomers. Some of the studies with maleic anhydride present physical evidence to support the claim that molecular complexes exist in these systems. The role, if any, played by these complexes in the polymerization is open to question. It has been argued[13,15] that the existence of molecular complexes in a reaction system does not prove they are the intermediates through which the reaction products are formed. It is possible that the relatively low equilibrium concentration of molecular complexes in these cases has no bearing on the polymerization and that polymerization occurs only with uncomplexed monomers.

With these points in mind, we have chosen to study the copolymerization of acrylonitrile–Lewis acid complexes with 1-hexene. These reactants have been reported[3] to lead to 1:1 copolymers. Under ordinary free-radical conditions, acrylonitrile and 1-hexene do not form copolymers.[3] Thus, complexing acrylonitrile with a Lewis acid causes a significant change in monomer reactivity ratios. If any type of molecular complex formation is responsible for such changes in reactivity, the effect should be clearly in evidence in this case.

Experimental Section

Infrared spectra of the polymers were obtained from a cast film on NaCl with a Perkin-Elmer Infracord. Solution spectra of

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acrylonitrile–Lewis acid complexes were obtained in methylene chloride solution using a cell with NaCl windows. Proton nmr spectra were obtained from polymer solutions in $CDCl_3$ and were recorded on a Varian Associates Model HA-100 spectrometer. All chemical shift data are reported relative to internal tetramethylsilane. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using matched quartz cells of 1.00- and 0.100-cm path lengths. The solution calorimeter was purchased from the Guild Corp., Bethel Park, Pa., and was identical with and operated in accordance with the descriptions given in the literature.[16] Elemental analyses and inherent viscosities were determined by standard procedures in the analytical department.

Materials. Acrylonitrile, methacrylonitrile, α-chloroacrylonitrile, and propionitrile were commercially available and were distilled under nitrogen from phosphorous pentoxide. Commercial 1-hexene was distilled under nitrogen. Reagent grade benzene and methylene chloride were refluxed over and distilled from calcium hydride. All the above materials were carefully stored under nitrogen in flasks equipped with three-way stopcocks. With that setup, samples can be withdrawn from the flask without exposure to the atmosphere through one arm of the stopcock by means of a syringe while a rapid stream of nitrogen is passed through the other arm of the stopcock. The gas chromatograms of all these materials showed only a single peak, and the materials are judged to be pure.

Boron trifluoride, boron trichloride, phenylboron dichloride, and triethylboron were commercially available in good quality and were used as obtained. Tetracyanoethylene was purchased and sublimed at 130° (30 mm) before use.

Preparation of Diethylaminoboron Dichloride. Boron trichloride (124 g) was dissolved in 500 ml of dry hexane and cooled to $-10°$. The solution was stirred mechanically and 155 g of diethylamine, also at $-10°$, was added dropwise. A precipitate of diethylamine hydrochloride was immediately formed. When addition was complete, the mixture was stirred for an additional hour and allowed to warm to room temperature. The hexane layer was separated and distilled under nitrogen. The fraction boiling at 60° (43 mm) was collected. The infrared spectrum of this material was consistent with that expected for the desired product.[17] The molecular weight was determined to be 162, which is in satisfactory agreement with the theoretical value of 154. The material was judged to be *ca.* 99% pure from its gas chromatogram.

Preparation of α-Acetoxyacrylonitrile. α-Acetoxyacrylonitrile was prepared according to the literature.[18] The material was purified by distillation prior to use.

Polymerization. A flask containing a magnetic stirring bar and 0.05 g of azobisisobutyronitrile was fitted with a three-way stopcock and carefully purged with nitrogen. A weighed amount of acrylonitrile was syringed into the flask through the stopcock while maintaining the nitrogen purge. The flask was then immersed in an ice bath and a volume of solvent containing the desired amount of Lewis acid was slowly added. The ice bath was removed and the desired weight of 1-hexene was added to the flask. The mixture was stirred for 24 hr and then poured into water and stirred. The organic layer was separated and washed with two portions of dilute aqueous base and dried over calcium chloride. The solvent was evaporated and the polymer dried to constant weight at 70° in a vacuum oven.

Stock solutions of all the Lewis acids used in this work except BF_3 could be prepared and used as described above. Boron trifluoride is only very slightly soluble in dry benzene or methylene chloride, and stock solutions could not be prepared. In this case, pure solvent was added to the reaction flask containing acrylonitrile and boron trifluoride was then added to the cooled solution until it was saturated. Analysis showed that an amount of BF_3 equivalent to the acrylonitrile was added to the solution by this technique. Additional acrylonitrile could then be added to the flask if less than a stoichiometric amount of BF_3 was required.

TABLE I
FORMATION CONSTANTS FOR COMPLEXES OF *p*-FLUOROBENZONITRILE

Acid	K_f
BCl_3[a]	$\geqslant 5000$
BF_3[a]	76 ± 20
$C_6H_5BCl_2$[a]	6 ± 0.6
$(CH_3)_3B$[a]	Very small
$(C_2H_5)_2NBCl_2$[b]	0

[a] Data from ref 19. [b] Value of K_f estimated by infrared spectroscopy.

Results and Discussion

The effect of monomer concentration ratios on the polymerization of acrylonitrile–Lewis acid complexes with α olefins has been studied,[3] and the results show that 1:1 copolymers are always prepared. Although several Lewis acids have been used as complexing agents for a number of polar monomers, no systematic study of the effect of Lewis acid strength on the reaction has been reported. To investigate this point, we have chosen the series of boron Lewis acids listed in Table I. The formation constants for complexes of these acids with *p*-fluorobenzonitrile have been determined[19] in methylene chloride solution and should parallel the formation constants for the corresponding acrylonitrile–Lewis acid systems. The compounds selected provide an acidity range of at least 10^3 as measured by the formation constants.

The behavior of diethylaminoboron dichloride with acrylonitrile was investigated by infrared spectroscopy. If a complex is formed, a shift in the infrared frequency of the nitrile band is observed from 4.5 to 4.4 μ, and an increase in the intensity of the band is noted. These observations were verified for all the acids in Table I which are known to complex nitriles. Infrared spectra of mixtures of diethylaminoboron dichloride and acrylonitrile in methylene chloride did not show any change in frequency or intensity of the nitrile band compared to binary mixtures of acrylonitrile and methylene chloride. It is therefore concluded that diethylaminoboron dichloride is too weak an acid to complex nitriles.

Data in Table II show the results of polymerizations of acrylonitrile and 1-hexene using the series of boron Lewis acids. It is immediately noticed that the analytical results for the polymers vary considerably. However, it was found extremely difficult to remove all the boron compounds from the polymer after the reaction was completed. For example, analysis of a polymer for boron and chlorine after repeated washing indicated 1.1% B and 1.5% Cl. If these values are added to the carbon, hydrogen, and nitrogen analyses for the same polymer, greater than 99.5% of the material was accounted for. Fluorine residues as high as 5.7% have been found in the polymer when boron trifluoride was used. This indicates the serious effect these residues can have on the analytical data. A number of different polymer isolation and purification methods were tried, but the procedure reported in the Experimental Section appeared to give the best results.

To minimize the effect of the Lewis acid contaminants on the analytical data, the nitrogen/carbon (N/C) ratio was used to judge the polymer composition, since this index will be independent of boron and halogen residues. The N/C values reported in Table II are not significantly different from the theoretical value of 0.13 and indicate that 1:1 copolymers

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TABLE II
POLYMERIZATION OF ACRYLONITRILE AND 1-HEXENE IN THE PRESENCE OF LEWIS ACIDS

AN,[a] g	1-Hexene, g	Acid	Acid/AN	Solvent	Time, hr	Polymer, g	η_{inh}, dl/g	% C	% H	% N	N/C[b]	$\frac{C\equiv N^c}{C=N}$
10.0	0.0	BF_3	1.0	CH_2Cl_2	72	2.1		63.2	6.0	22.2	0.35	
4.8	16.8	BF_3	1.0	CH_2Cl_2	24	2.1		66.2	10.1	7.6	0.12	0.61
4.8	16.8	BF_3	0.5	CH_2Cl_2	24	1.0		63.6	10.5	7.0	0.11	0.47
2.4	6.7	BCl_3	0.5	CH_2Cl_2	24	1.2		74.0	10.5	11.2	0.15	1.1
2.4	6.7	BCl_3	1.0	CH_2Cl_2	24	3.7		75.3	10.7	9.4	0.13	1.2
2.4	9.6	BCl_3	1.0	C_6H_6	24	2.8	0.17	76.3	10.6	9.3	0.12	1.7
2.4	9.6	BF_3	1.0	C_6H_6	24	0.4		71.4	10.1	8.8	0.12	1.5
2.6	7.5	$C_6H_5Cl_2$	1.0	C_6H_6	24	2.0	0.20	77.0	10.9	10.0	0.13	3.3
3.0	10.1	$(C_2H_5)_3B$	1.0	CH_2Cl_2	24	1.7		61.2	13.1	8.9	0.14	0.43
3.0	10.1	$(CH_5)_3B$	1.0	C_6H_6	24	1.9		54.1	10.5	9.0	0.17	
2.4	9.6	$(C_2H_5)NBCl_2$	1.0	C_6H_6	24	0						

[a] Acrylonitrile. [b] The nitrogen/carbon ratio (N/C) for 1:1 acrylonitrile–hexene copolymers is 0.13. The elemental analysis for a 1:1 copolymer is 78.9% C, 10.9% H, and 10.2% N. [c] Absorbance ratio for nitrile/imine bands in polymer spectra.

TABLE III
POLYMERIZATION[a] OF α-SUBSTITUTED ACRYLONITRILES WITH 1-HEXENE IN THE PRESENCE OF BCl_3

Monomer,[b] g	1-Hexene, g	Polymer, g	% C	% H	% N	N/C[c]	Infrared functional groups
MAN (2.5)	5.8	0.24	72.3	10.7	6.4	0.089	$C\equiv N$, $C=C=N$, $C=N$
CAN (3.0)	5.8	0.84	61.0	8.1	6.5	0.11	$C\equiv N$ (very weak), $C=N$
CAN (3.0)	5.8	1.18	41.4	6.9	5.3	0.13	$C\equiv N$ (very weak), $C=N$
ANOAc (2.5)	3.8	0.94	62.4	7.6	3.4	0.055	$C\equiv N$, $C=N$, OH
ANOAc (2.5)	3.8	0.73	52.9	7.6	5.0	0.094	$C\equiv N$ (very weak), $C=N$, OH

[a] Polymerization conditions were the same for each example. Benzene was used as the solvent and molar equivalents of BCl_3 and polar monomers were used. [b] Abbreviations mean: MAN, methacrylonitrile; CAN, chloroacrylonitrile; ANOAc, acetoxyacrylonitrile. [c] N/C ratios for 1:1 copolymers are: MAN/1-hexene, 0.12; CAN/1-hexene, 0.13; ANOAc/1-hexene, 0.11.

were prepared in every case. These results show that the strength of the Lewis acid does not affect the composition of the polymer, provided it is strong enough to complex the nitrile group. No polymer was prepared when diethylaminoboron dichloride was used. This is the only acid incapable of complexing acrylonitrile. The fact that no polymer was made in this case suggests that the uncomplexed diethylaminoboron dichloride may have trapped radicals formed from azobisisobutyronitrile and prevented initiation. In all cases, we found it necessary to use a free-radical initiator to obtain polymer. No evidence for spontaneous polymerization was observed if the reaction system were anhydrous. Addition of microliter quantities of water to the reaction medium catalyzed polymerization, presumably by a cationic mechanism. These polymers, however, were low molecular weight greases and were obtained in very low conversion.

The data in Table II also show that 1:1 copolymers can be prepared with less than a stoichiometric amount of Lewis acid. This, however, leads to lower yields of polymer. A change in solvent for the polymerization from methylene chloride to benzene had no effect on the yield of polymer or the apparent rate of polymerization. These are interesting results and will be discussed in a later section of this paper. It is also interesting to note that the rate of homopolymerization of the acrylonitrile–boron trifluoride complex is apparently much slower than copolymerization with 1-hexene. Higher monomer charges and longer reaction times are required to obtain yields of polyacrylonitrile equivalent to that of the 1:1 copolymer.

Data for the copolymerization of boron trichloride complexes of substituted acrylonitrile monomers with 1-hexene are presented in Table III. The N/C ratios show that chloroacrylonitrile and 1-hexene copolymerize to give 1:1 copolymers. The data for methacrylonitrile and acetoxyacrylonitrile, however, are much less conclusive. The N/C ratios in these cases are at variance with the calculated values for 1:1 copolymers. The infrared spectra of the acetoxyacrylonitrile–1-hexene copolymers show only a very weak carbonyl band and a strong hydroxyl band. These results suggest that secondary reactions, presumably between the Lewis acid and the ester function, lead to modification of the polymer. Because of this no reliable conclusion regarding the polymer composition can be made.

Structure of the Copolymer. The infrared spectra of all the copolymers prepared had the expected bands for the nitrile stretching frequency and methylene stretching, bending, and rocking frequencies. In addition, broad intense bands at 6.0 μ, characteristic of $C=N$ groups,[20] were observed in the polymer spectra. We interpret this as evidence of 1,2 addition to the nitrile group during polymerization. Without careful standardization of an infrared method, accurate measurement of the relative amounts of the nitrile and imine functional groups in the polymer is impossible. However, it does appear[21] that 1,2 addition has occured to a significant fraction of the nitrile groups. The infrared spectrum of the methacrylonitrile–1-hexene copolymer contained still another band at 5.0 μ which is characteristic[20] of cumulated double bonds in compounds such as allenes, ketenes, and isocyanates. This indicates that some 1,4 addition to methacrylonitrile

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[20] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, pp 265–267, 269.

[21] The extinction coefficient for $C=N$ in aliphatic imines is on the order of 140 (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1959, p 271) and that for benzonitrile is *ca.* 50 [C. D. Ritchie, *et al.*, *J. Amer. Chem. Soc.*, **84**, 4687 (1962)]. With the aid of these extinction coefficients and the absorbance ratios for the nitrile/imine functions reported in Table II, we estimate that from 10 to 40% of the nitrile groups in the polymer have undergone 1,2 addition.

TABLE IV

NMR SPECTRA OF ACRYLONITRILE–1-HEXENE COPOLYMERS

δ,[a] ppm	Assignment
0.92	Methyl protons on butyl ends
1.34	Methylene protons in butyl side chains
1.66	Methylene protons in backbone
1.84	Methine proton adjacent to butyl side chain + allyl protons
2.70	Methine protons adjacent to nitrile

[a] Shift data obtained in $CDCl_3$ solution relative to internal TMS.

occurred leading to the C=C=N structure. Apparently, the methyl group provides sufficient steric hindrance to make 1,4 addition competitive with 1,2 addition.

The nmr spectra of the acrylonitrile–1-hexene copolymers are reported in Table IV along with the assignments for each signal. The spectra are what would be expected for 1:1 copolymers. Allylic protons which must be present in the polymer, due to 1,2 addition to the nitrile, are most likely obscured by signals at 1.84 ppm which are assigned to the methine protons adjacent to the butyl side chain. Strong overlap of that signal by those at 1.66 and 1.34 ppm precludes accurate integration of these peaks. The signals at 0.92 and 2.70 ppm have relative areas of 3:1, as would be expected from their assignments and the composition of the polymers. No evidence of vinyl protons was observed in the nmr spectra. From this we conclude that there is no significant number of pendant vinyl groups in the polymer and, therefore, the polymer must be branched at points where 1,2 addition to the nitrile occurred. A reference spectrum of polyacrylonitrile showed that methylene groups in the backbone of that polymer displayed signals at 2.25 ppm. The spectrum of acrylonitrile-1-hexene polymers does not show an absorption at that frequency, and we conclude that there are no acrylonitrile dyads in the copolymer.

This evidence strongly points to a 1:1 alternating acrylonitrile copolymer. This result is far different from that expected with ordinary free-radical polymerization. The cause of the selective alternation in this case is intriguing and bears investigation. Popular explanations tend to attribute such selectivity to the formation of 1:1 molecular complexes of the Lewis acid complex and the α olefin.

The Search for Molecular Complexes. We have endeavored to obtain physical evidence for molecular complexes between acrylonitrile–Lewis acid complexes and 1-hexene in order to gain an understanding of this polymerization. Our first attempts were to study mixtures of the acrylonitrile–Lewis acid complexes with 1-hexene in methylene chloride by ultraviolet spectroscopy. These results were inconclusive. If anything, only end absorptions were observed in the ultraviolet region, and these were generally difficult to reproduce. We conclude that these end absorptions were due to very low conversion to polymer which was initiated by adventitious water. In addition, the ultraviolet solvent cut-off (*ca.* 235 mμ) of methylene chloride prohibits examination of the solutions below that point. It is possible that the charge-transfer transition for the system under study could be in the far-ultraviolet. It is also known[22] that the absence of a charge-transfer spectrum does not rule out a molecular complex as a possible reaction intermediate. Because of this ambiguity with optical approaches to the problem, we chose to study this matter calorimetrically.

TABLE V

HEAT OF SOLUTION OF BENZENE AND *p*-XYLENE IN TCNE[a]–CH_2Cl_2

Solvent	Solute	$-\Delta H_{soln}$, cal/mol	$-\Delta H_f$,[b] kcal/mol	K_f,[c] calcd	K_f,[d] lit.
CH_2Cl_2	Benzene	22 ± 9			
3.0×10^{-2} *M* TCNE[e]	Benzene	42 ± 10	2.3	0.3	0.28
CH_2Cl_2	*p*-Xylene	97 ± 10			
3.1×10^{-2} *M* TCNE[e]	*p*-Xylene	180 ± 10	3.4	1.0	1.1

[a] Tetracyanoethylene. [b] Data from ref 23. [c] Formation constant of TCNE molecular complex calculated from heat of solution data and ΔH_f. [d] Data from ref 24. [e] Methylene chloride solutions.

If a molecular complex is formed by mixing 1-hexene and the acrylonitrile–boron trifluoride complex, the heat of solution of 1-hexene in a solution of the acrylonitrile–boron trifluoride complex should be more exothermic than the heat of solution of 1-hexene in a model solvent. The excess heat would be due to formation of the molecular complex. We have chosen solutions of the propionitrile–boron trifluoride complex in methylene chloride as the model solvent, since they should closely approximate the acrylonitrile–boron trifluoride solutions. An important difference is that propionitrile does not contain a double bond and cannot act as an electron acceptor in the formation of molecular complexes.

To demonstrate that this technique is capable of detecting the modest energy changes associated with complex formation, we have determined the heats of solution of benzene and *p*-xylene in tetracyanoethylene solutions. Both aromatic compounds are known[23,24] to form complexes with tetracyanoethylene. Because the tetracyanoethylene solutions were dilute, pure methylene chloride was used as the reference solvent. The results are compiled in Table V. More exothermic heats of solution were observed in tetracyanoethylene solution than in pure methylene chloride with either benzene or *p*-xylene. To show consistency, we have used the difference in the heat of solution in tetracyanoethylene and methylene chloride and literature values for the heat of complex formation to estimate the concentration of the molecular complex. From this an estimate of the formation constant of the molecular complex was made and satisfactory agreement with literature values was obtained. These results show that the calorimetric method can detect complex formation.

Table VI summarizes data for the heat of solution of 1-hexene in solutions of the propionitrile–boron trifluoride complex and the acrylonitrile–boron trifluoride complex.

TABLE VI

HEAT OF SOLUTION OF 1-HEXENE

Solvent	ΔH_{soln}, cal/mol
CH_2Cl_2	950 ± 20
0.50 *M* PrN:BF_3[a]	710 ± 20
0.56 *M* AN:BF_3[b]	670 ± 20
1.0 *M* PrN:BF_3[a]	600 ± 40
1.0 *M* AN:BF_3[b]	760 ± 70
2.0 *M* PrN:BF_3[a]	870 ± 20
2.2 *M* AN:BF_3[b]	860 ± 30

[a] Propionitrile–boron trifluoride complex in CH_2Cl_2. [b] Acrylonitrile–boron trifluoride complex in CH_2Cl_2.

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Much higher concentrations of acceptor were used in this case so that interactions could be detected between 1-hexene and the acceptor even if they were weaker than those for the tetracyanoethylene–benzene complex. The heat of solution data pass through a minimum[25] as the concentration of either the acrylonitrile–boron trifluoride complex or the pripionitrile–boron trifluoride complex increases. This parallel behavior strongly suggests that the mode of interaction between 1-hexene and either of the Lewis acid complexes is quite similar. Since the data show no appreciable differences for the heat of solution of 1-hexene in either solvent system up to the 2 *M* acceptor level, there cannot be any significant interaction with the double bond of acrylonitrile. Such an interaction would be required for the formation of a molecular complex. We are confident that a difference of 100 cal between the heat of solution of 1-hexene in the acrylonitrile–boron trifluoride solution and that in the propionitrile–boron trifluoride solution could be detected. With the concentrations used and assuming a heat of formation of about 2 kcal/mol, we estimate that a molecular complex with a formation constant $\geq 10^{-3}$ could be detected. Very weak complexes with formation constants less than 10^{-3} are not likely intermediates, since no change was observed in the reaction when benzene, instead of methylene chloride, was used as a polymerization solvent.

Benzene is certainly a much better donor molecule than 1-hexene and would be expected to form stronger complexes with the acrylonitrile–Lewis acid acceptors. If such complexes were important intermediates in the polymerization, a severe rate-retarding effect and perhaps a change in the polymer composition would be expected. This, however, was not observed. In addition, it was found that, even though there is a high selectivity in the polymerization leading to 1:1 alternating copolymers, the mode of addition of monomers is not specific. The observed addition to the nitrile group as well as addition to the carbon–carbon double bond are evidence of the nonspecific nature of propagation. Kosower[22] and Banthorpe[15] have reviewed criteria for molecular and π complexes as reaction intermediates. They concluded that high specificity in the reaction products, resulting from geometric requirements of the complex, is necessary to support claims that these species are important to the reaction mechanism.

Conclusions

In view of the experimental results, it is clear that ground-state molecular complexes of the acrylonitrile–Lewis acid complexes and 1-hexene are not important features of the reaction mechanism. Even so, a very high selectivity is evident in the propagation step. The underlying reasons for this selectivity are still obscure, although the known facts can be accounted for by a reaction scheme similar to that originally proposed by Walling.[11] In that scheme no specific complex between monomers is involved and, therefore, no major solvent effect on the copolymerization would be expected on changing from methylene chloride to benzene. Similarly, no significant differences would be expected for the heat of solution of 1-hexene in solutions of acrylonitrile or propionitrile Lewis acid complexes. In addition, the propagating species would be free to react with either the carbon–carbon double bond of acrylonitrile or the nitrile group. In this way, the nonspecific addition of acrylonitrile in the polymer, which leads to the formation of imine groups, can be accounted for along with the 1:1 alternating structure of the polymer.

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(25) The observation of such extrema is not without precedent. The origin of such effects, however, is still the subject of investigation and remains unresolved; *cf.* E. M. Arnett, M. Ho, and L. L. Schalezer, *J. Amer. Chem. Soc.*, **92**, 7039, (1970), and references cited therein.