is strongly dependent on the transformations of "living" chains during their deactivation offer a good explanation of our experimental results as well as of those obtained by other authors[8,9] on the variation of MWD with conversion.

In the case of low polymerization degrees, with "living" chains being associated and hence mainly undergoing recombination in the course of deactivation, the MWD of poly(butadienes) formed is uninodal (Figure 2, curve 1) and is characterized by very high monodispersity (K = 1.04, Table I). The high homogeneity of *trans*-1,4-poly(butadienes) supports the conclusion that reactions which limit the chain growth do not occur and that the difference in the rate of addition of the first and subsequent butadiene units is very small.

With increasing degree of conversion the dissociation of dimeric "living" chains is observed and monomeric forms enter into deactivation along with dimers; as a result, the MWD becomes binodal. Each peak of summerized distribution represents an independent narrow symmetric distribution. In principle, at high degrees of conversion when the dimers of "living" chains are dissociated for the most part, the MWD should again become unimodal, as it was observed in ref 8.

The difference between gel permeation chromatograms of *trans*-1,4-poly(butadienes) recorded by us and those given in ref 8 (disappearance of binodal distribution in the latter case and its appearance in our chromatograms with increasing conversion) is apparent and can be explained by our studies of the process of polymer formation with the polymerization degree not higher than 40 while in ref 8 the lowest polymerization degree of *trans*-1,4-poly(butadiene) was about 50, hence, the chromatograms complement each other nicely.

Formally, the polymerization of butadiene with bis(π-crotylnickel iodide) resembles the polymerization in the presence of bifunctional initiators giving "living" chains with two growing chains in media containing some or no impurities which prevent macromolecules from growing at one end. The variations of MWD in these systems[20,21] are very much like those observed in the present study.

The investigation performed is a good illustration of great possibilities offered by combination of radiochemical and MWD studies in clarifying the fine specific features of polymerizations carried out in the presence of organometallic catalysts.

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Kinetics and Mechanism of the Initial Stages in the Bis(π-crotylnickel iodide)-Catalyzed Polymerization of Butadiene

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ABSTRACT: Using the ^1H NMR technique a kinetic study has been made of the active centers formation and initial stages of polymer chain propagation in the polymerization of 1,1,4,4-tetradeuteriobutadiene with bis(π-crotyl-d_6-nickel iodide). The fact that the orders of these reactions are close to unity is explained by dimeric forms of the catalyst complexes taking part in the reactions.

Studies on transformations of 1,3-dienes under the action of bis(π-crotylnickel halides) made it possible to establish some regularities which contribute to fundamental understanding of the mechanism of ionic coordination polymerization. Of the observed phenomena the most interesting are the following: the dependence of the catalyst stereoselectivity in the formation of cis-1,4 and trans-1,4 structures on the nature of halogen atom bound to nickel[1–3] and the ability of iodide complexes to initiate the formation of *trans*-1,4-poly(dienes) in an aqueous medium[3,4] which is not observed with other organometallic catalysts except for the butadiene polymerization by Rh(III) salts.[5]

Investigation of the reaction between butadiene and bis(π-crotylnickel iodide) in the medium containing Lewis bases showed that by their effect on the polymerization the Lewis bases can be subdivided into two clearly defined groups. The first one comprises σ donors which irrespective of their σ-donor ability exert no influence on the rate and direction of the polymerization, and the second one comprises compounds possessing both σ-donor and π-acceptor ability. Depending on their π-accepting power these compounds can lower the polymer yield or, in the limit, suppress the butadiene polymerization. Based on these facts the unique ability of bis(π-crotylnickel iodide) to initiate stereoselective polymerization of 1,3-diolefins in the presence of water has been explained not only by hydrolytic stability of the nickel–carbon bond (in the absence of oxygen) but also by the dative bonding of the transition metal with a substrate playing a significant role along with the donor–acceptor interaction in the transition state of the reaction. Taking into account the d^8 character of the nickel atom in bis(π-crotylnickel iodide), a high bond strength Ni–I, strong trans effect of the iodide anion, and the diolefin molecules entering into the metal coordination sphere, the preference has been given by us to the five-coordination transition state formed with the participation of the nickel p_z orbital.[3,4]

The diolefin polymerization initiated by bis(π-crotylnickel iodide) proceeds at rates which allow the individual stages of the process to be observed by means of NMR spectroscopy; in particular, the addition of the first and next monomer molecules,[6–8] the anti-syn isomerization of the adducts formed,[9] etc.

In the present paper, an attempt has been made using NMR technique to quantitatively evaluate the kinetics of elementary stages of bis(π-crotylnickel iodide) addition to butadiene. Based on the data obtained the polymerization mechanism is discussed. To simplify at most the ^{1}H NMR spectra of the reacting system and to provide a great accuracy of measurements, bis(π-crotyl-d_6-nickel iodide) (with the proton at the methyl group) and 1,1,4,4-tetradeuteriobutadiene are used as model compounds.

Experimental Section

1,1,4,4-Tetradeuteriobutadiene was prepared by the known method[10] by decomposing $C_4H_2D_4SO_2$ under argon at 140°. The latter was synthesized by treating the nondeuterated analogue with D_2O in an absolute dioxane in the presence of 0.5 mol of K_2CO_3 at 30°. $C_4H_2D_4SO_2$ was freed of impurities by a twofold recrystallization from methanol. According to the NMR data the content of butadiene-d_4 exceeded 98%.

Bis(π-crotyl-d_6-nickel iodide) was prepared from nickel carbonyl and crotyl-d_6 iodide by the method in ref 11. The latter was synthesized from perdeuteriobutadiene[12] and freshly prepared 57% hydroiodic acid.

The reaction of $(C_4D_6HNiI)_2$ with $C_4H_2D_4$ was carried out in 9-mm diameter glass reactors with a dividing wall preheated under vacuum at 250° to remove moisture and oxygen occluded on the reactor walls. Into the upper part of the reactor having a striker, butadiene-d_4 dried over calcium hydride was reevaporated under vacuum. The amount of butadiene charged was determined by weighing with the help of an analytical balance. Into the bottom of the reactor the benzene solutions of $(C_4D_6HNiI)_2$ and $Si(CH_3)_4$ were introduced from Schlenk vessels. Reactors were sealed and kept in solid CO_2 until measurements were performed.

^{1}H NMR spectra were recorded on a HX-90 Brucker spectrometer in 10-mm rotating ampoules wherein the reactor was placed. Chemical shifts were measured using tetramethylsilane as an internal standard. To increase the signal-to-noise ratio the multiple signal accumulation was carried out. Specific integral intensities of signals were determined by dividing the area of resonance due to the corresponding proton by the area of resonance due to $Si(CH_3)_4$ protons. The molar concentration of I–IV complexes and the amount of the monomer consumed in reactions leading to their formation (M_n) at a given moment were calculated from the formula:

$$M_n = \frac{I_{H_t}}{I_{CD_2H}} \cdot C_0$$

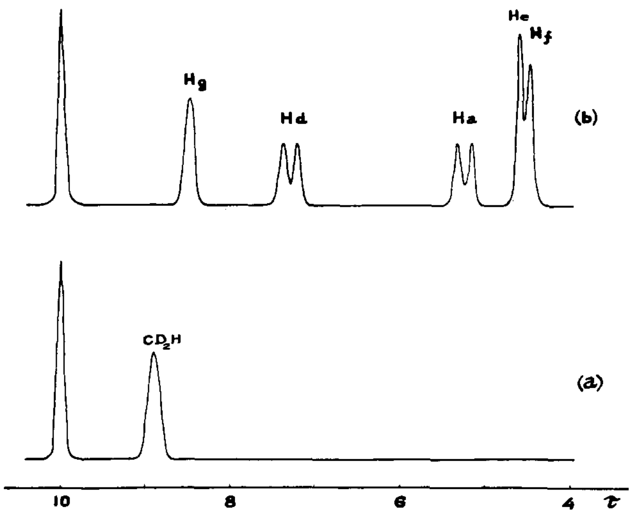


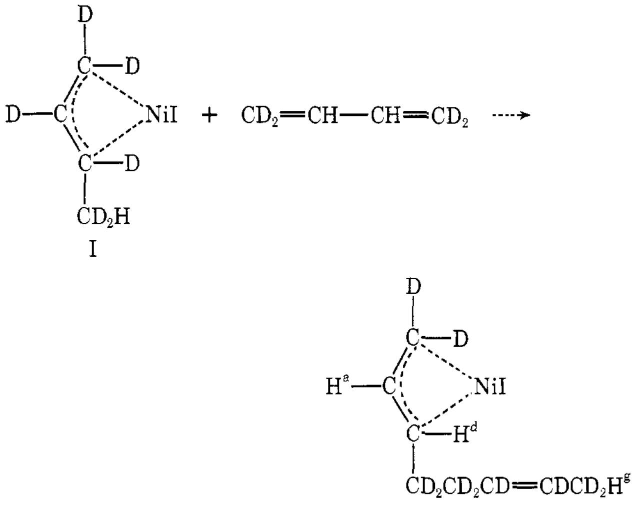
Figure 1. ^{1}H NMR spectra of $(C_4D_6HNiI)_2$ (a) and of its reaction products with $C_4H_2D_4$ (b).

where I_{H_t} is the integral intensity of signal from one of the protons of the I–IV complexes at each instant of time; I_{CD_2H} is the initial integral intensity of signal from proton in complex I; C_0 is the initial concentration of complex I in the reaction medium (mol/l.).

Measurements were performed at 20 ± 1°. The concentration of I based on nickel was varied between 0.133 and 0.423 mol/l. The initial concentration of $C_4H_2D_4$ in all experiments was 2.50 mol/l.

Results

The ^{1}H NMR spectrum of bis(π-crotyl-d_6-nickel iodide) (I) shows only one singlet resonance at τ 8.9 corresponding to the proton of the *syn*-CD_2H group (Figure 1a). The addition of the first molecule of 1,1,4,4-tetradeuteriobutadiene results in the formation of complex II whose spectrum already shows three signals: doublets from the methine protons H^a (τ 5.25) and H^d (τ 7.3) of the syn-π-allylic unit (J_{ad} = 13 Hz) and from proton H^g (τ 8.5) of the displaced π-crotyl-d_6 ligand (Figure 1b).



Kinetic data for the reaction of II formation can be obtained from the changes in the integral intensities of a signal from a proton of complex I, which is diminished at τ 8.9, or of one of the signals from H^a or H^d protons of compound II, which is increased with time.

Interaction between II and a molecule of butadiene-d_4 does not naturally change the intensities of signals from H^a and H^d protons, but it leads to the appearance of a new sig-

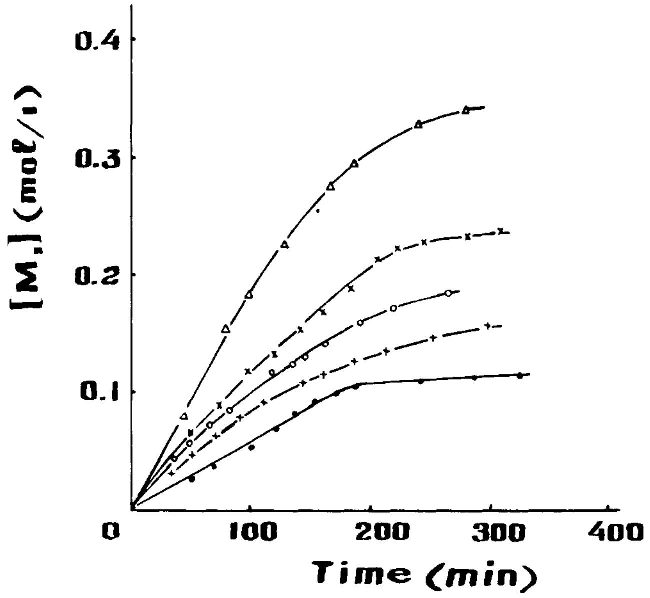
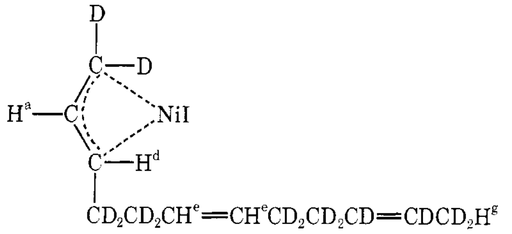


Figure 2. Kinetic curves of the complex II formation. Initial concentration, [$C_4H_2D_4$] = 2.5 mol/l.; [Ni] (mol/l.); (●) 0.133; (+) 0.173; (○) 0.212; (X) 0.250; (△) 0.423.

nal from methine protons H^e (τ 4.6) of displaced π-crotyl-d_4 unit (complex III):

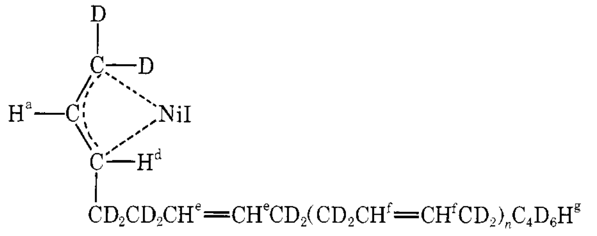
II + $CD_2{=}CH{-}CH{=}CD_2 \longrightarrow$



III

Further removal of this unit from the nickel atom due to subsequent insertion of $C_4H_2D_4$ results in the appearance of H^f protons of complex IV, whose signals are shifted to a lower field by 0.1 ppm as compared with signals from H^e protons.

III + $nCD_2{=}CH{-}CH{=}CD_2 \longrightarrow$



IV

Kinetic curves for the reactions of III and IV complexes formation can be plotted on the basis of changes in the integral intensities of signals from H^e and H^f protons (τ 4.5–4.6).

Signals of complex II appeared in the ^1H NMR spectrum of the reaction mixture just after the contact between I and butadiene-d_4. At the first period the rate of II formation is the highest, its value being dependent on the initial concentration of I. Figure 2 shows the kinetic curves for the complex II formation at various initial concentrations of I. In all cases the amount of the complex II formed will reach its limiting value, the initial concentration of I, which indicates that all the molecules of I are involved in the reaction with butadiene. Some time after the beginning of the reaction, there appear signals of complexes III and IV in the spectra. The shape of kinetic curves of these complexes formation evidences that complex III has formed from complex II (Figure 3).

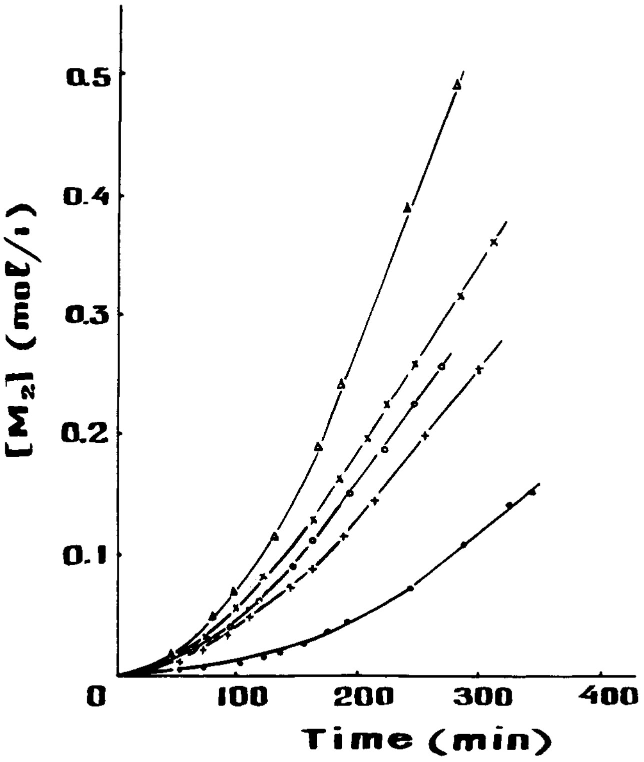


Figure 3. Kinetic curves of the polymer chain propagation. Initial concentrations are the same as in Figure 2.

In Figures 4 and 5 the dependences of the II and III + IV complex formation rates on the momentary concentrations of I and II respectively are plotted in logarithmic coordinates. Angular coefficients of the slope of both straight lines imply approximately the first order of these reactions in I and II. The reaction constants, calculated from sections cut off on the ordinate axes in Figures 4 and 5, are: K_{II} = 0.0027 l./(mol min) and K_{III+IV} = 0.0036 l./(mol min).

Discussion

Results of kinetic studies carried out by soviet authors[13-15] and reproduced in ref 16 and 17 have shown that the rate of the polymerization of butadiene by dimeric bis(π-allylnickel iodides) is proportional to the concentrations of a monomer and π-allylic complex to the power from 0.5 to 1. In all cases the observed reaction rate orders in catalyst are explained as being due to the participation of its monomeric forms in propagation. In this case, the half-order of the reaction corresponds to the conditions under which the concentration of monomeric forms is very low, while the first order is observed at very strong dissociation of the dimer.

Our results may not be attributed to the strong dissociation of bis(π-crotylnickel iodide) into monomeric form, because in our experiments the concentrations of a starting complex were by 2–4 orders higher than those used in ref 13–17, the butadiene concentrations being quite similar. Under the conditions of our experiments the monomeric form of π-allylnickel iodide is most probably present in negligible concentrations.

First order of the complex II formation with respect to I

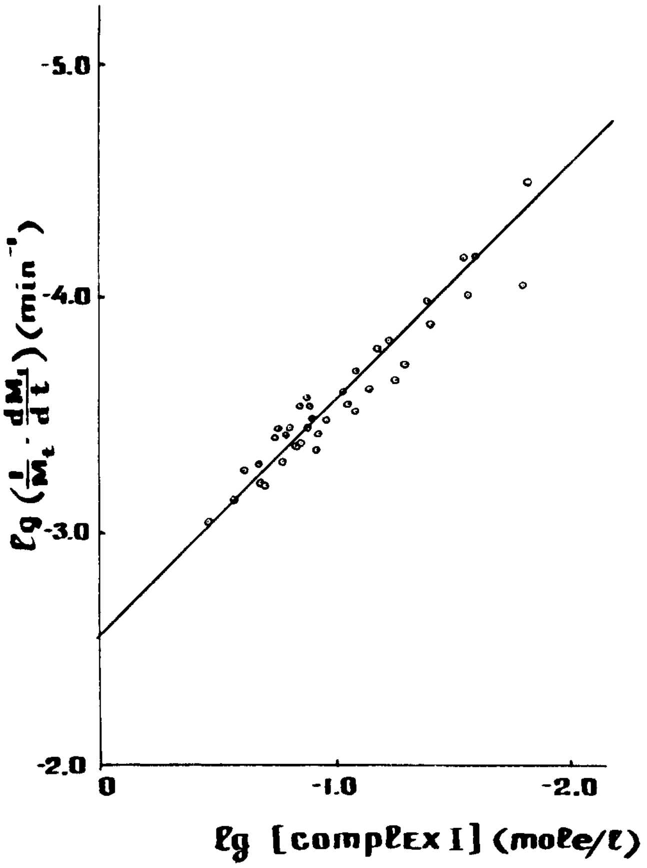


Figure 4. Dependence of initiation rate on the momentary concentration of catalyst (complex I): M_1, butadiene consumed for the complex (II) formation. M_t, momentary concentration of butadiene.

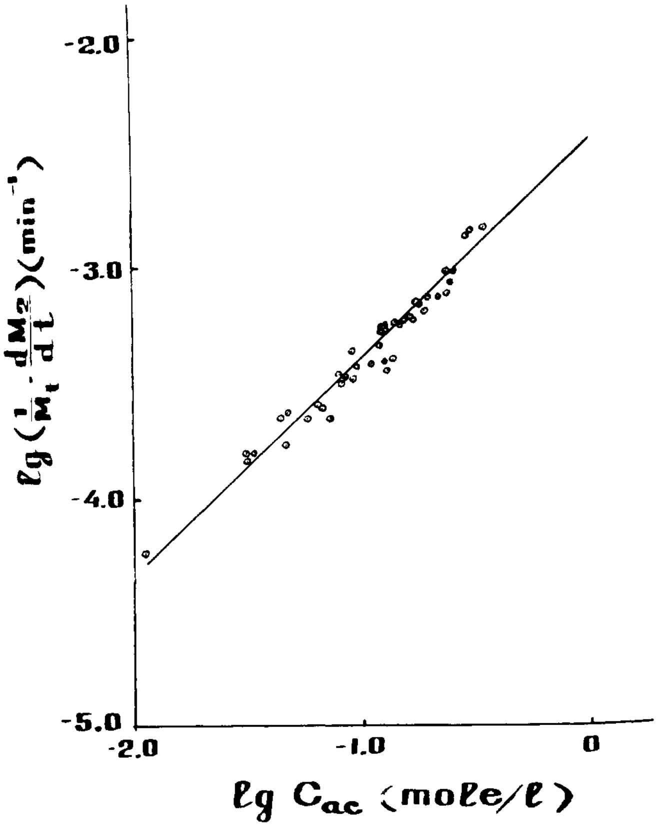


Figure 5. Dependence of propagation rate on the concentration of active centers (C_{ac}): M_2, butadiene consumed for the complexes III and IV formation.

under our experimental conditions indicates that it is just the dimeric form of bis(π-crotylnickel iodide) that is active in the reaction of the first molecule of butadiene addition. Since all the π-crotyl-d_6 ligands are gradually removed from the nickel atom as diolefin inserts, it is clear that every atom of the transition metal dimer takes part in the interaction.

Reaction of the complex II formation can be treated as the reaction of initiation, while the complex II itself can be treated as the active center of the polymerization process. In this case the subsequent insertion of butadiene would be the reaction of polymer chain propagation. Such a treatment is quite competent, as the complex II differs from the starting bis(π-crotylnickel iodide) in the structure of its organic ligands which are bound to the nickel atom not only with π-allylic but also with π bond. The existence of the latter is evidenced by the difference in chemical shifts of H^e and H^f protons.

First order of the reaction of propagation, that is of the complexes III and IV formation (at least, 1-3 acts of insertion) with respect to active centers, suggests that this reaction proceeds via a mechanism similar to that of initiation reaction, i.e., the active centers involved in the process are also in dimeric form.

In that way, the results of our investigation lend further support to our earlier assumption[3,4] about the activity of the dimeric form of bis(π-crotylnickel iodide) in the polymerization of butadiene and about the five-coordination transition state. Taking into account the results of other studies,[13-17] it seems reasonable to suggest the dual character of bis(π-crotylnickel iodide) reactivity, which depending upon polymerization conditions manifests itself in the preferential participation of dimeric or dissociated forms of the complex in the reactions of polymer chain propagation. Theoretically, the monomeric π-crotylnickel iodide, due to its higher coordination unsaturation, should display higher activity than dimer. But in cases when the concentration of dimeric complex (as in our experimental conditions) is sufficient to enable its lower activity to be compensated for, this complex becomes capable of competing with the monomeric form in the reactions of diolefin addition. The latter should be favored also by donor–dative interaction between the nickel atom and diolefin, which plays an important role in the case of dimer. It is known that dative bonding contributes to the lowering of activation energy of the reactions of transition metals and various ligands,[18] which accounts for the unique aptitude of bis(π-crotylnickel iodide) to produce *trans*-1,4-poly(butadienes) in aqueous media and in the presence of strong σ donors. The failure of bis(π-crotylnickel iodide) to undergo reactions with pure σ donors is further substantiated by the absence of any changes in the ^1H NMR spectrum of $(C_4H_7NiI)_2$ when triphenylamine was added to it.

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Chemical Modification of Polymers. VIII. Reaction of Quinoline Reissert Compounds (1-Acyl-1,2-dihydroquinaldonitriles) with Polymeric Halides and Aldehydes

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ABSTRACT: The quinoline Reissert compound reacts with poly(vinylbenzyl chloride) to about 70% conversion. Upon hydrolysis to the fully aromatic quinoline the resultant polymer is insoluble, presumably because of cross-linking. A soluble polymer results when the hydrolysis is carried out in the presence of phenol. Because the chloro groups are replaced by phenoxy moieties, the cross-linking is presumably circumvented. The quinoline Reissert compound also condenses with polymeric aldehydes in essentially quantitative conversion. Reactivity patterns of the quinoline Reissert compound vis-á-vis the isoquinoline Reissert compound are rationalized on the basis of the principle of hard and soft acids and bases.

Like other chemists, polymer chemists seek to alter the physical and chemical properties of molecules to optimize them for a particular end use. Traditionally this has been achieved by varying the structure of the monomers which are polymerized. An alternate approach is to modify chemically a pre-formed polymer. Until recently this tack was not followed to any great extent. In recent years, however, the chemical modification of polymers has received increasing attention.[1-4] Much of the work has dealt with insoluble polymers as reagents, growing from the protein synthesis matrix developed by Merrifield.[5]

We, too, have been interested in chemical modifications of polymers[6-12] as a means of controlably altering physicochemical characteristics. Our work has centered on soluble polymers because they are of greater utility for us and because they allow further insight into reaction processes.[10]

This approach to structure variation offers the following advantages: (1) it is possible to synthesize polymers that cannot be prepared by direct polymerization techniques[10] or only with difficulty; (2) a series of structurally related polymers of constant degree of polymerization, namely that of the starting polymer, can be prepared; (3) a series of structurally related polymers of constant tacticity, replicating that of the parent polymer, can be produced; (4) copolymers of desired composition can be prepared by stoichiometric control of sequential reactions.

We have reported the attachment of aza-aromatic moieties to polymers bearing haloalkyl[8,11] and formyl functions.[9,12] The two processes involved the use of an isoquinoline Reissert compound, namely 2-benzoyl-1,2-dihydroisoquinaldonitrile (**1**). This was reacted via the anion **2** with poly(vinylbenzyl chloride) (**3**) to give polymer **4**, which can be hydrolyzed to the aromatic system **5** in essentially quantitative conversion. **2** also reacts with polymeric aldehydes such as **6** to afford polymeric esters such as **8**. **8** was formed