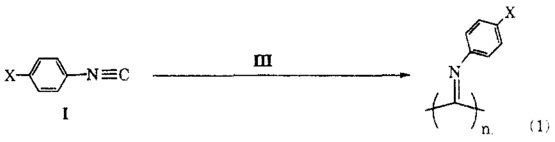
Use of Copolymerization Phenomena in Mechanistic Studies: Monomer Substituent Effects in Nickel-Catalyzed Isocyanide Polymerizations

Timothy J. Deming and Bruce M. Novak*,†

Department of Chemistry, University of California at Berkeley, and the Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

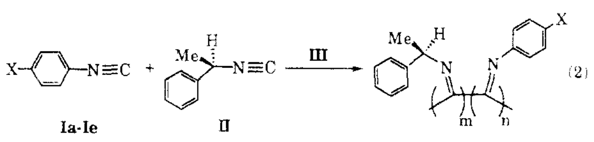
Received July 6, 1993
Revised Manuscript Received August 20, 1993

Our recently developed system for the living polymerization of isocyanides[1] using transition-metal catalysts was achieved through a detailed mechanistic understanding of the chain growth process.[2] In an effort to further refine this system, we sought additional means of probing the nature of the active specie(s) in the reactions. Since, under both oxygen and nitrogen atmospheres, there are varying (and sometimes considerable) amounts of charge developed in the transition states of the chain propagation steps,[2] we wanted to examine the effects that substituents on the monomer would have on these reactions.[3] Toward this goal we synthesized a variety of phenyl isocyanide monomers (**Ia–e**) which were substituted in the *para* position (eq 1).[4] In trying to measure propagation rate constants we encountered a problem in that a majority of these homopolymerizations were heterogeneous and gelled at low conversions so that accurate kinetic data could not be acquired. Our solution was to set up copolymerizations of these monomers with the comonomer (*R*)-1-phenylethyl isocyanide (**II**)[4] and determine propagation rate constants of the aryl monomers from the well-behaved copolymerization reactions (eq 2).



(1)

	Ia	Ib	Ic	Id	Ie
X =	–N(CH$_3$)$_2$	–OCH$_3$	–CH$_3$	–H	–CF$_3$
σ =	-0.83	-0.27	-0.17	0.00	+0.54



(2)

Monomer **II** undergoes living polymerization with the catalyst, $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$ (**III**), we have used for these studies.[5] The polymerization is very well behaved and produces polymer which is soluble in the reaction solvent (toluene) at molecular weights up to 500 000 (we have used the pure enantiomer in these studies to avoid stereoselection effects which would complicate the reaction kinetics).[6] We thought that copolymerization of aryl isocyanides with this monomer would solubilize the reaction mixture by bringing the poly(aryl isocyanide) chains into solution.[7] Also, the aryl isocyanides do not undergo living polymerization but chain transfer extensively, and so the addition of **II** would hopefully reduce deleterious side reactions associated with chain transfer (free-radical chemistry).[2]

To construct a Hammett σ–ρ plot,[8] it was necessary to obtain either the homopolymerization rate constants of insertion of an aryl isocyanide into a polymer chain with an ultimate aryl iminoacyl group (k_{ArAr}) or the reactivity ratios of the aryl monomers relative to the constant comonomer (r_{Ar}).[9] In this polymerization system we were fortunate in that **II** was considerably less reactive *in competition* with the aryl isocyanides (although they have comparable rate constants for homopolymerization).[10] This was determined by simultaneous measurement of monomer concentrations versus time which showed that only *ca.* 15% of **II** was polymerized at >85% conversion of any of the aryl isocyanides (Figure 1). These kinetic data show that, if the polymerization of both monomers is living, then a taper block copolymer and not a random copolymer will be produced. If the rate equations for loss of aryl isocyanide under nitrogen and oxygen atmospheres (eqs 3 and 4) are examined, an assumption can be made that, since $k_{II} \ll k_{Ar}$, very few catalyst centers are present with **II** ultimate groups ([**II**–cat] $\approx$ 0). Therefore, it follows that most active sites contain aryl iminoacyl ultimate groups and [Ar–cat] $\approx$ [cat]$_0$ ([cat]$_0$ = initial catalyst concentration). The approximated rate expressions that result from this assumption are those given below (eqs 5 and 6) in which the desired quantity, k_{ArAr}, can be determined directly without the need to measure reactivity ratios.

$$\text{Under } N_2\text{:} \quad \frac{-d[\text{ArNC}]}{dt} = k_{ArAr}[\text{ArNC}][\text{Ar-cat}] + k_{ArII}[\text{ArNC}][\textbf{II}\text{-cat}] \tag{3}$$

$$\text{Under } O_2\text{:} \quad \frac{-d[\text{ArNC}]}{dt} = k_{ArAr}[\text{Ar-cat}] + k_{ArII}[\textbf{II}\text{-cat}] \tag{4}$$

$$\text{Under } N_2\text{:} \quad \frac{-d[\text{ArNC}]}{dt} \approx k_{ArAr}[\text{ArNC}][\text{cat}]_0 \tag{5}$$

$$\text{Under } O_2\text{:} \quad \frac{-d[\text{ArNC}]}{dt} \approx k_{ArAr}[\text{cat}]_0 \tag{6}$$

The validity of this kinetic approximation was checked by two methods. First, we examined the copolymers using gel permeation chromatography (GPC) to verify that the aryl isocyanide polymerizes almost exclusively in the first phase of the polymerization, and then, upon depletion of aryl isocyanide, polymerization of **II** ensues. The distribution observed for all aryl isocyanide copolymerizations was bimodal, containing a narrow high molecular weight peak and a broad low molecular weight peak (Figure 2). If these were true copolymerizations or block copolymerizations, only a single peak for the copolymer would be expected. The cause of the bimodal distribution is simply that aryl isocyanides undergo chain-transfer reactions while **II** does not.[2,5] Hence, at the beginning of the reaction aryl isocyanide polymerizes almost exclusively, chain transferring to produce a low molecular weight polymer of broad molecular weight distribution. This polymeric product consists almost entirely (*ca.* 85%) of aryl monomer and is therefore almost a pure homopolymer. After consumption of the aryl isocyanide, **II** remains almost exclusively in the reaction mixture which then undergoes living polymerization to produce a high molecular weight polymer of narrow molecular weight distribution. This polymeric product consists primarily of **II** and is also almost pure homopolymer. Selective extraction of the low molecular weight oligomer from the high molecular weight polymer and NMR analysis of the resulting fractions revealed that the monomers were indeed mostly

---

† Presidential Faculty Fellow, Alfred P. Sloan Fellow.

0024-9297/93/2226-7092$04.00/0

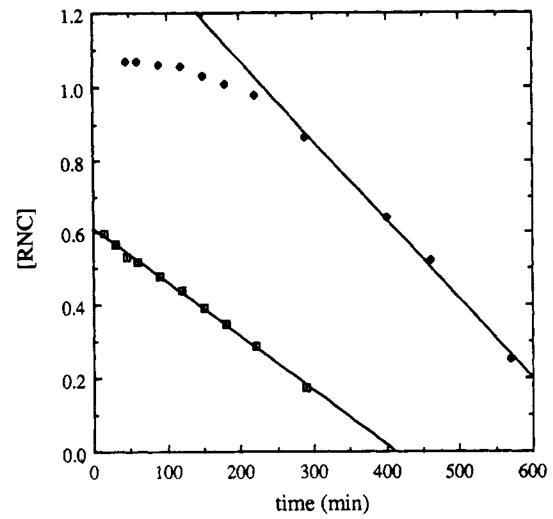


Figure 1. Loss of monomer versus time for a feed mixture of 70% **II** and 30% **Id** using **III** under oxygen. The white squares are for **Id**, and the black diamonds are for **II**.

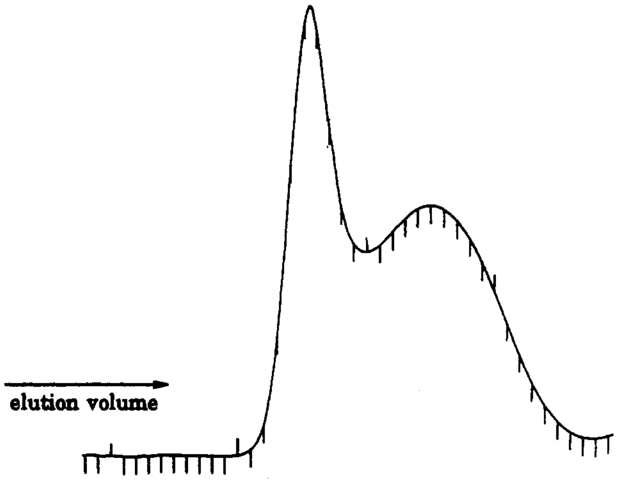
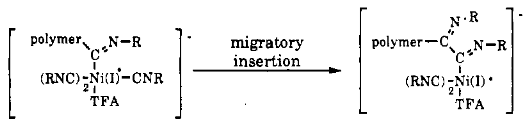


Figure 2. GPC trace of the polymer produced from a feed mixture of 70% **II** and 30% **Id** using **III** under oxygen.

partitioned into the different fractions as predicted. Hence, by the nature of the relative propagation rate constants and the chain transfer reactions which occur, the polymers produced from these "copolymerizations" are more correctly viewed as mixtures of homopolymers with some comonomer contamination.

The second method used to check the kinetic assumption was comparison of k_{ArAr} from copolymerization data with one which could be accurately measured in a homopolymerization reaction: that for **Ib** since this polymerization remains homogeneous. k_{ArAr} for the copolymerization (50% w/w each monomer) under oxygen was found to be 1.5 (2) × 10^{-2} s^{-1}, and k_{ArAr} for the homopolymerization was found to be 1.3 (1) × 10^{-2} s^{-1}: the values are the same within experimental error. Since our assumption appeared valid, we utilized this convenient procedure for measuring k_{ArAr} to collect the data required to construct Hammett plots under both nitrogen and oxygen atmospheres (Figure 3). We note that determination of rate constants at a different initial composition (30% aryl isocyanide) gave ρ values which were identical to those in Figure 2 within experimental error.

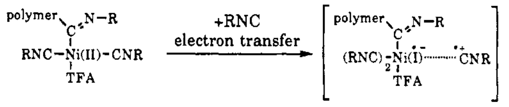
We have shown that the nickel-catalyzed polymerization of isocyanides undergoes a mechanism change upon changing from a nitrogen to an oxygen atmosphere.[5] As can be seen from Figure 3, this is likewise reflected in the effects of monomer substituents on the rate-determining step of the propagation reaction. Under oxygen, we have proposed that the rate-determining step for chain propagation involves a migratory insertion reaction at an anionic nickel(I) center (eq 7).[2] In this step, since the



(7)

metal center is electron rich (anionic) and insertion reactions are facilitated by Lewis acidic centers, electron-withdrawing ligands (i.e., coordinated monomers) should greatly facilitate the reaction and ρ should be positive. This can be visualized by drawing analogy to the carboxylate ligand in **III**: when acetate is replaced with highly electron-withdrawing trifluoroacetate, the rate of polymerization increases tremendously.[11]

Under nitrogen, we have proposed the rate-determining step shown in eq 8 where the metal center is reduced from



(8)

nickel(II) to nickel(I) by an incoming isocyanide.[2] Here electron-withdrawing groups on the coordinated isocyanides and in the polymer chain should favor the reaction (positive ρ), yet electron-withdrawing groups on the isocyanide which is oxidized would strongly *disfavor* this reaction (negative ρ). The observed negative ρ illustrates that this isocyanide oxidation process is electronically very significant in this reaction mechanism.

We have demonstrated that "copolymerization" reactions in polyisocyanide synthesis can be used to easily extract otherwise only difficultly obtainable kinetic data. These data in turn were used to verify the predicted role that monomer plays in the nickel-mediated polymerization of isocyanides.

Acknowledgment. We gratefully acknowledge financial support for this work from the National Science Foundation and industrial PYI donors. T.J.D. and B.M.N. acknowledge the NSF for a graduate student fellowship and a Presidential Faculty Fellowship (PFF) Award, respectively.

Supplementary Material Available: Experimental procedures for general manipulations and for all of the polymerization

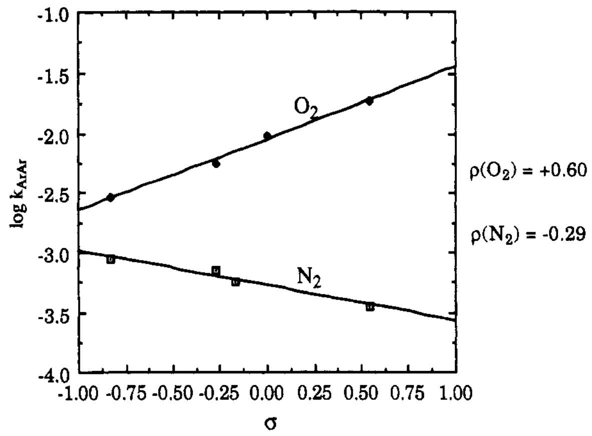


Figure 3. Hammett plot for substituent effects on the monomer under both nitrogen and oxygen atmospheres using **III** catalyst. Composition is 50% by weight of each monomer.

kinetics (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For general references on polyisocyanides, see: (a) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30. (b) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C. *Macromolecules* **1988**, *21*, 1839. (c) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 326. (d) Millich, F. *Chem. Rev.* **1972**, *72*, 101. (e) Millich, F.; Sinclair, R. G., II *J. Polym. Sci., Part C* **1968**, *22*, 33. (f) Millich, F. *Adv. Polym. Sci.* **1975**, *19*, 117. (g) Millich, F. *Macromol. Rev.* **1980**, *15*, 207.

(2) (a) Deming, T. J.; Novak, B. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 885. (b) Deming, T. J.; Novak, B. M. submitted for publication in *J. Am. Chem. Soc.*

(3) Substituent effects in isocyanide polymerizations have been studied previously using a $BF_3 \cdot Et_2O$ catalyst system. (a) Yamamoto, Y.; Takizawa, T.; Hagihara, N. *Nippon Kagaku Zasshi* **1966**, *87*, 1355. (b) Yamamoto, Y.; Hagihara, N. *Nippon Kagaku Zasshi* **1968**, *89*, 898. Since the Ni catalysis studied here follows a completely different mechanism, the Japanese results have no relation to those reported here.

(4) (a) Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472. (b) Ugi, I.; Meyr, R. *Chem. Ber.* **1960**, *93*, 239.

(5) (a) Deming, T. J.; Novak, B. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 455. (b) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 6043.

(6) (a) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 4400. (b) Deming, T. J.; Novak, B. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 641–2.

(7) King, R. B. *Polym. News* **1987**, *12*, 166.

(8) (a) Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1. (b) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91. (c) Levitt, L. S.; Widing, H. F. *Prog. Phys. Org. Chem.* **1976**, *12*, 119. (d) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

(9) (a) Meyer, V. E. *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 2819. (b) Van Der Meer, R.; Van Gorp, E. H. M.; German, A. L. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1489. (c) Otsu, T. *Makromol. Chem., Macromol. Symp.* **1987**, *10*/*11*, 235.

(10) Chenvanij, J. Ph.D. Thesis, University of Missouri, Kansas City, MO, 1973.

(11) Dawans, F.; Teyssie, Ph. *J. Polym. Sci., Part B* **1969**, *7*, 111.

(12) Dawans, F.; Marechal, J. C.; Teyssie, P. *J. Organomet. Chem.* **1970**, *21*, 259.