TABLE III

Feed[a]	Copolymer[a]
0.12	2.88
0.29	2.94
0.43	2.83
1.0	3.01

[a] Moles of acrylamide per mole of SO_2.

chloride–sulfur dioxide system[14] in that both give polymers with variable compositions generally containing less sulfur dioxide as the polymerization temperature is increased. The increased amount of sulfur found in the acrylamide–sulfur dioxide copolymer from the 100° run as compared to the polymer from the 80° run is at variance with this trend. The reason for this anomaly is not known. Another similarity to the vinyl chloride system is the absence of much effect, if any, of the feed ratio on the compositions of the polymers formed at room temperature (Table III).

Acknowledgment. We thank members of the Scientific Services Department for the infrared data, elemental analyses, and viscosity data. O. Francesconi helped with the polymerizations done at 80 and 100°, and H. Ando translated some Japanese reports. This project was undertaken at the request of Dr. H. P. Panzer of the Industrial Chemicals and Plastics Division of the American Cyanamid Co.

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Influence of Added Oxidants on the π-Crotylnickel Iodide Catalyzed Polymerization of Butadiene

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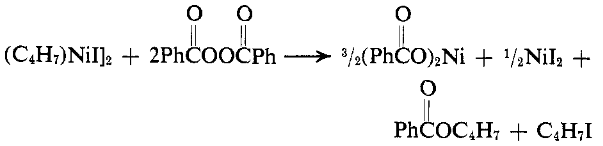
It has been suggested that such additives as oxygen, peroxides, or iodine may influence the activity and stereospecificity of π-crotylnickel halides as butadiene polymerization catalysts.[1–3] We report a series of experiments with crotylnickel iodide which indicate that oxygen, peroxides, and molecular iodine simply destroy the catalyst to produce inactive products. The experiments relate to the effects of the latter additives on the rate of butadiene polymerization, the activation energy of the reaction, and the molecular weights of polymers produced.

Results and Discussion

The effect of added benzoyl peroxide on the rate of butadiene polymerization at constant nickel concentration is shown in Figure 1. In these reactions the catalyst was pretreated with peroxide prior to introduction of monomer. The points shown are experimental rates, while the curve is a theoretical trace calculated on the assumption that catalyst is destroyed according to the reaction

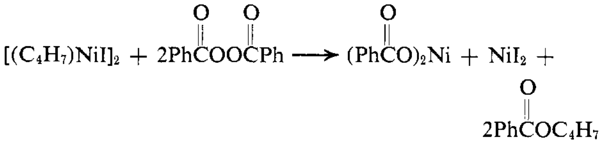


$$(C_4H_7)NiI]_2 + 2\mathrm{Ph\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}Ph} \longrightarrow {}^3/_2(\mathrm{Ph\overset{O}{\overset{\|}{C}}})_2Ni + {}^1/_2NiI_2 + \mathrm{Ph\overset{O}{\overset{\|}{C}}OC_4H_7} + C_4H_7I \quad (1)$$

and the rate law for the polymerization is[4]

$$\text{rate} = k_p(k_2/k_{-2})^{1/2}[(C_4H_7NiI)_2]^{1/2}[\text{monpmer}] \quad (2)$$

Reaction 1 is written as an exact analog of the reaction of phenylmagnesium bromide with benzoyl peroxide.[5] The insoluble nickel salt produced in (1) gave an experimental iodide to benzoate ratio more consistent with the above stoichiometry than that of reaction 3. The close correspondence of the experimental points to the calculated curve of Figure 1 leaves little doubt that the benzoyl peroxide is simply destroying the crotylnickel iodide dimer on a two-to-one molar basis. Similar results were obtained for molecular oxygen and iodine. The latter reagent destroyed crotylnickel iodide dimer on a 1:2 molar basis, but difficulties in measuring small quantities of oxygen made accurate determination of the stoichiometry of its reaction with crotylnickel iodide difficult. The effect of O_2 on polymerization rate is illustrated in Figure 2. It may be reasonably assumed that the apparent stoichiometry of 0.3 mol of O_2 per mole of nickel actually corresponds to reaction 4, where the products are totally inactive.



$$[(C_4H_7)NiI]_2 + 2\mathrm{Ph\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}Ph} \longrightarrow (\mathrm{Ph\overset{O}{\overset{\|}{C}}})_2Ni + NiI_2 + 2\mathrm{Ph\overset{O}{\overset{\|}{C}}OC_4H_7} \quad (3)$$

$$2[(C_4H_7)NiI]_2 + O_2 \longrightarrow \text{products} \quad (4)$$

In a second series of experiments a sample of catalyst was partially destroyed by reaction with benzoyl peroxide and the resulting catalyst was used to determine the activation energy of the polymerization reaction. The temperature coefficient was identical with that obtained with unadulterated catalyst, and when account was taken of destruction of the catalyst according to (1), the Arrhenius plots for pure catalyst and catalyst–benzoyl peroxide reactions were superimposable within experimental error, as shown in Figure 3.

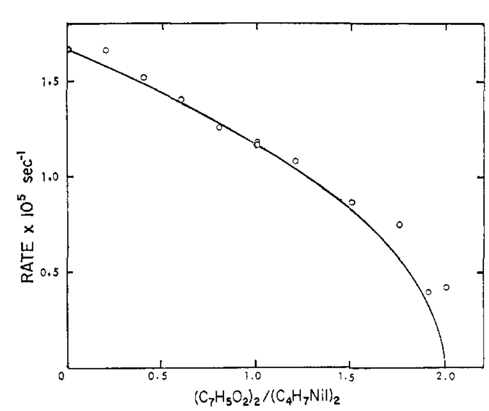


Figure 1. Effect of added benzoyl peroxide on the apparent rate coefficient (rate/[C_4H_6]); [$(C_4H_7NiI)_2$] = 0.005 *M*, [C_4H_6] = 1.5 *M*, temperature = 50°: O, experimental points; ———, computed curve.

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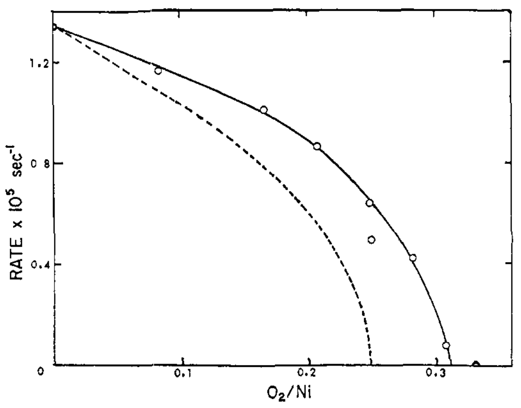

Figure 2. Effect of added oxygen on the apparent rate coefficient; $[(\mathrm{C_4H_7NiI})_2] = 0.005\ M$, $[\mathrm{C_4H_6}] = 1.5\ M$, temperature = 50°: ○, experimental points; ----, computed curve assuming eq 4.

The third experimental test involved a study of the effects of additives on molecular weight. We previously reported a theoretical relationship among degree of polymerization ($\overline{\mathrm{DP}}_n$), catalyst concentration, and conversion.[4] A more detailed investigation has revealed that the true expression is that shown below.

$$\frac{1}{\overline{\mathrm{DP}}_n} = \frac{2\alpha[(\mathrm{C_4H_7NiI})_2]}{\text{conversion}} + \frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} \qquad (5)$$

Equation 5 differs from our original equation by the factor α, which has a value close to (probably equal to) 0.5.[6] For the moment we are merely concerned with the fact that $(\overline{\mathrm{DP}}_n)^{-1}$ is proportional to [catalyst] and to (conversion)$^{-1}$. Figure 4 shows a plot of $(\overline{\mathrm{DP}}_n)^{-1}$ *vs.* (conversion)$^{-1}$ for an unadulterated system and for a system where catalyst was partially destroyed by benzoyl peroxide. When corrected for destruction of catalyst according to (1), the latter data fitted the same curve as the data from the unadulterated system. The same was true for reactions where catalyst was partially killed by oxygen or iodine.

Most of the data reported herein were obtained from reactions where the catalyst was pretreated with additive. The reactions of benzoyl peroxide and iodine were very rapid, and both appear to provide suitable reactions for assay of allylnickel halides. The reaction of oxygen was much slower and even after prereaction times of many minutes, a slight deceleration was observed during the subsequent polymerization reaction. In systems where additive was pretreated with catalyst, we could detect no difference in the microstructure of the resulting polymers from that of a polymer produced with unadulterated catalyst. In reactions where additives were introduced during polymerization, a slight increase in cis content was observed in the resulting polymers. We attribute this result to the fact that reactions 1 and 4 proceed by a radical mechanism; thus, they introduce a certain amount of radical polymerized polybutadiene if they are carried out in the presence of monomer.

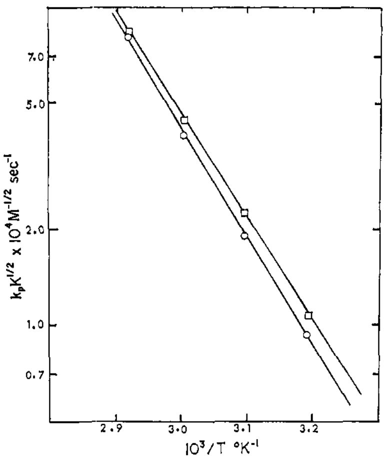

Figure 3. Arrhenius plots for ○, pure $[(\mathrm{C_4H_7})\mathrm{NiI}]_2$ catalyst and □, a 1:1 benzoyl peroxide:$[(\mathrm{C_4H_7})\mathrm{NiI}]_2$ catalyst.

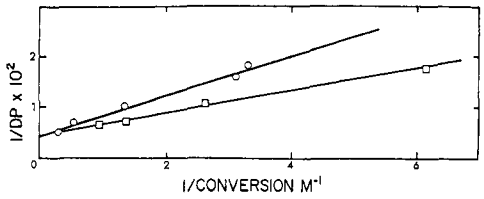

Figure 4. Dependence of $(\overline{\mathrm{DP}})^{-1}$ on (conversion)$^{-1}$: ○, pure $[(\mathrm{C_4H_7})\mathrm{NiI}]_2$ (slope = 0.0039 *M*, $[(\mathrm{C_4H_7NiI})_2] = 0.0039\ M$) and □, a 1:1 benzoyl peroxide: $[(\mathrm{C_4H_7})\mathrm{NiI}]_2$ catalyst (slope = 0.0022 *M*, active $[(\mathrm{C_4H_7NiI})_2] = 0.0024\ M$, reacted $[(\mathrm{C_4H_7NiI})_2] = 0.0049\ M$).

In conclusion, we would like to emphasize that there is no doubt that certain additives, particularly those of the Lewis acid or base type, have profound effects of the activity and stereospecificity of π-allylnickel halide catalysts. On the other hand, additives whose electron affinity is high enough to oxidize the coordinated allyl ligand to an allyl radical appear only to destroy the catalyst. Radicals generated during the destruction of the catalyst may initiate some polymerization and give an apparent change in stereospecificity.

Experimental Section

Preparation of catalyst and rate measurement have been described previously.[4] Furukawa and associates prepared the crotylnickel halide catalysts according to the method of Fischer and Buerger.[7] This is an inferior technique giving low yield and impure product,[8] and this may explain the discrepancy between our work and that of Furukawa.

Molecular weights were determined using a Waters Associates gel permeation chromatograph with columns of 10^2, 4 × 10^2, 10^3, and 10^4 Å porosity. The columns were calibrated with monodisperse polystyrene standards obtained from Waters Associates. Number-average molecular weights of polybutadienes determined by gel permeation chromatography agreed within ±5% with values determined by vapor pressure osmometry (vpo). The $\bar{M}_n$ values determined by vpo were used to calculate the molecular weight per unit equivalent extended chain length (*Q*) for polybutadiene. The value $Q = 20 \pm 2.3$ agreed closely with that deduced by other workers for gel permeation chromatography calibration for polybutadiene.[9,10]

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