# Isocyanate Resins from Amide Copolymers

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## Synopsis

Useful isocyanate-containing polymers may be made by reacting amide copolymers with a hypo-chlorite such as sodium hypochlorite. A highly branched carbon structure adjacent to the amide is required, otherwise the isocyanate is lost through reaction with components of the reaction mixture. The polymeric isocyanates react rapidly with monomeric and polyamines and at adequate rates with hydroxyl compounds. These polymers are very useful in paint films and other applications due to their ability to udergo crosslinking and chain extensions by reaction of the isocyanate groups.

## INTRODUCTION

It has been known for a long time that primary amide groups react with sodium hypochlorite and other hypohalites to produce primary amines, i.e., the Hofmann reaction. Hofmann[1] showed in 1882 that the formation of isocyanate groups was an essential step in the sequence of reactions leading to amine formation. With very rare exceptions,[2–5] isocyanates have not been prepared by this method because they react immediately with other materials in the reaction mixture such as water and alcohols.

Where isocyanates have been successfully prepared by the Hofmann reaction, the amide group has been attached to a tertiary carbon. By "tertiary carbon" is meant a carbon atom with three other carbons attached to it in addition to the amide group. Apparently, the reaction rate of the isocyanate is reduced by the steric hindrance of the carbon chain branches.

This observation has been confirmed by attempting to prepare isocyanates from compounds with amide groups attached to "primary," "secondary," and "tertiary" carbons. Adipamide and stearamide gave isocyanate yields of zero to around 1% of theory. A 16% yield of isocyanate was recovered from 2-pentanamide, and a 75% yield was recovered from Versatic amide. Versatic amide is a mixture of isomeric ten-carbon compounds where the amide group is attached to a tertiary carbon.

Further work was done to learn if these trends applied to amide-containing polymers. Previous workers[6–9] have applied the Hofmann reaction to amide homopolymers such as polyacrylamide and polymethacrylamide and have isolated no isocyanate-containing polymers. These authors suggest that any isocyanate intermediates produced react quickly with adjacent functional groups on the polymer chain. Copolymers and terpolymers may be made where one of the monomers contains a primary amide group. Polymers of this type may
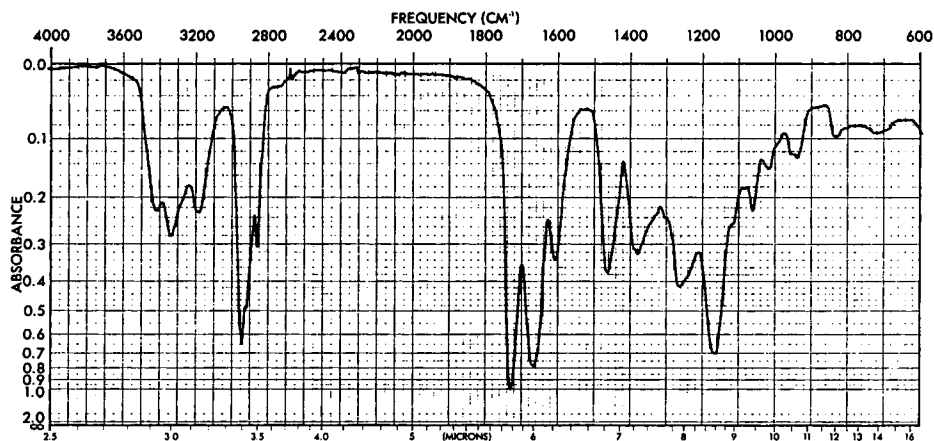
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Fig. 1. Infrared spectrum of methacrylamide–butyl acrylate copolymer.

or may not contain a high percentage of isolated amide groups relative to adjacent amide groups. This work indicates that such amide copolymers react in a manner analogous to the monomeric amide compounds. When subjected to the Hofmann reaction, acrylamide copolymers, "secondary carbon" amides, have been found to give fairly good yields of isocyanate, but it is difficult to preserve the isocyanate for a long enough time to allow for separation and purification procedures. It is mostly lost by reaction with water or other components of the reaction mixture before they can be removed. A considerable amount of crosslinking must occur because a well-gelled resin mass usually forms while one is trying to distill out the water.

Methacrylamide copolymers, "tertiary carbon" amides, have been found to give good yields of isocyanate which may be recovered in a stable form and which presents no gelling and crosslinking problems.

## EXPERIMENTAL

### Preparation of a 30% Methacrylamide–70% Butylacrylate Copolymer

Two solutions were prepared. Solution A consisted of 54 g azobisisobutyronitrile in 1278 g cellosolve acetate. Solution B consisted of 750 g isopropanol, 270 g methacrylamide, 630 g butyl acrylate, and 18 g lauryl mercaptan. The isopropanol was required to dissolve the methacrylamide. Solution A was put into a 5-liter reaction flask and heated to 75°C. Solution B was then added continuously, with stirring, over a 4-hr period while refluxing the mixture. During the addition, the reflux temperature progressively lowered from 92°C to 75°C. It was then refluxed for 3 more hours. To remove the isopropanol, the solution was vacuum distilled at near 50 torr and 60°C. As the volume of the resin solution was reduced by distillation, additional cellosolve acetate was added from time to time to replace the distillate. Distillation was continued until no isopropanol could be seen in the infrared spectra of the distillate. A total of 900 ml of distillate was replaced with cellosolve acetate. The resulting resin solution contained 29.3% solids, its viscosity was 240 centipoises at 25°C, and its acid equivalent was 0.018 meq/g.
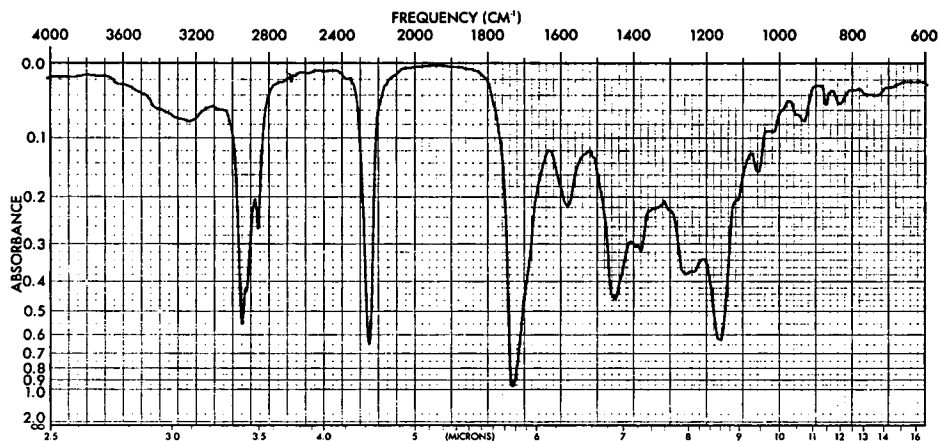
Fig. 2. Infrared spectrum of isocyanate copolymer.

The molecular weight of the resin was studied by gel permeation chromatography.  A sample of the resin was freed of solvent, dissolved in tetrahydrofuran, and passed through microstyragel columns.  The GPC curve showed a rather broad molecular weight distribution.  The number-average molecular weight, 1900 g/mole, and weight-average molecular weight, 5700 g/mole, were calculated from the GPC data.

Nitrogen analysis by the Kjeldahl method showed slightly more than theory for the methacrylamide copolymer.  This indicates little or no imide formation. Figure 1 shows the infrared spectra of a dry film of the copolymer.  The characteristic amide bands are seen in the 3200 to 3500 cm$^{-1}$ region and at 1670 cm$^{-1}$ and 1610 cm$^{-1}$.

## Preparation of Isocyanate Resin from Methacrylamide–Butylacrylate Copolymer

A 5-liter three-neck flask was fitted with an addition funnel, mechanical stirrer, and thermometer and set in a refrigerated water bath.  The above resin solution, 1608 g, was put into the flask with 749 g toluene, and 997 g (841 ml) of a 4.0$N$ sodium hypochlorite solution was put into the addition funnel (1.01 mole/mole amide).  The sodium hypochlorite solution was added in small portions over a 2.3-hr period.  The hypochlorite reaction is exothermic, and it was added at a rate which would produce an average temperature near 6°C.  A stable emulsion was formed almost immediately on mixing in the sodium hypochlorite, and a considerable reduction in viscosity was seen as the reaction progressed.  Small samples were taken periodically from the reactor and examined by infrared spectra to follow the progress of the reaction.

The reactor was arranged for heating, and the temperature was increased to 30°C and held there for 50 min.  During this period, the pH of the emulsion dropped from 10.4 to 9.2.  The emulsion was acidified with hydrochloric acid to pH 5.0 to protect the isocyanate groups and to promote emulsion breaking. An emulsion breaking agent, tetradecyldimethylbenzylammonium chloride was stirred in.  After sitting about 1 hr, the emulsion had separated and the water layer of 1080 g was discarded.  The resin phase was vacuum distilled to remove

residual water and excess solvent, and finally filtered to remove a small amount of precipitated sodium chloride.

The properties of the isocyanate resin solution were: solids, 32.1%; viscosity, 150 centipoises at 25°C; and acid equivalent, 0.688 meq/g. The nitrogen content of resin (Kjeldahl analysis) was 5.83% (5.76% theory). Figure 2 shows an infrared spectrum of a dry film of the resin. The isocyanate content is shown by the strong band near 2260 cm$^{-1}$. The spectrum also shows that the amide bands have been removed by the sodium hypochlorite reaction.

Titration analysis of the resin by the amine equivalent method gave 5.24% NCO, thus an equivalent weight of 800 g/mole NCO.

### Preparation of a Methacrylamide–Styrene–Ethyl Acrylate Terpolymer

A resin was prepared by polymerizing together 225 g methacrylamide, 600 g styrene, and 675 g ethyl acrylate, thus a monomer ratio of 15% methacrylamide, 40% styrene, and 45% ethyl acrylate. These monomers were mixed with 900 g *tert*-butyl alcohol and 180 g of a 50% solution of *tert*-butyl peroctoate. A solvent mixture consisting of 210 g cellosolve acetate and 210 g toluene was put into the reactor and heated to 69°C. The monomer mixture was added to this over a 4-hr period while maintaining the temperature between 102° and 91°C. The mixture was refluxed an additional 3 hr at 91°C.

The properties of the resin solution were: solids, 50.8%; acid equivalent, 0.0107 meq/g; and viscosity, 15,000 centipoises at 25°C.

### Isocyanate Resin from the Methacrylamide–Styrene–Ethyl Acrylate Terpolymer

A 5-liter, three-neck flask was fitted with a stirrer, addition funnel, thermometer, reflux condenser, and suitable means for heating and cooling. The above resin solution, 1620 g, and 1008 g toluene were put into the flask and stirred well. Then, 1260 g of a 4.0 N sodium hypochlorite solution (1.46 mole of NaOCl per methacrylamide) was added through the addition funnel over a 2-hr period. Heat from the exothermic reaction was removed using a pan of cold water while keeping the reaction temperature between 30° and 32°C. After all of the sodium hypochlorite was added, 76 g 12N hydrochloric acid was stirred in to neutralize the excess sodium hydroxide in the sodium hypochlorite solution. This was followed by 18 g trimethyllaurylammonium chloride. This is a surface-active agent used to break the emulsion which exists at this stage. After sitting for 1 hr, the emulsion has separated, and the lower aqueous layer which had formed was withdrawn through a dip tube. It had a pH of 5.7.

During the sodium hypochlorite addition, small samples were withdrawn periodically for isocyanate analysis by infrared spectra.

The resin layer was then vacuum distilled to remove alcohol and water from the solution. The distillation was done at 50 to 60 torr pressure and 30° to 65°C during a period of less than 2 hr. Distillation was continued until the infrared spectra of the distillate showed it to be free of alcohol and water. Finally, the resin solution was filtered through filter paper to remove sodium chloride and any other suspended matter. The properties of the isocyanate resin solution were: solids, 53.3%; viscosity, 550 centipoises at 25°C; acid equivalent, 0.157

meq/g. Isocyanate content of the resin by the amine equivalent method was 5.30% NCO. This indicates a 72% conversion of amide to isocyanate.

### Reaction of Isocyanate Resins with Amines

An isocyanate resin solution similar to the terpolymer resin above was used. A small molar excess of $n$-butyl amine was stirred into the resin solution at room temperature. An infrared spectrum taken three minutes later showed a complete absence of isocyanate and the appearance of a new pair of bands at 1550 cm$^{-1}$ and 1640 cm$^{-1}$. This pair of bands appears to be characteristic of ureas from "tertiary carbon" isocyanates.

A molar excess of 2-ethylhexylamine was stirred with a sample of the isocyanate resin at room temperature. An infrared spectrum taken 8 min later showed a complete absence of isocyanate and the appearance of the urea bands. Thus, these isocyanate resins react very rapidly with amines. This reactivity shows that the amine equivalent method of analysis is applicable. Various isocyanate resins prepared as described above were mixed with polyamines including ethylenediamine and hexamethylenediamine. Within a few minutes at room temperatures, stiff, strong gels formed. This indicates rapid crosslinking of the resin through urea linkages. The ability of these resins to crosslink with amines was utilized to form tough, quick-curing paint films.

### Reaction of Isocyanate Resins with Hydroxyl Compounds

The above-described isocyanate resins were mixed with various hydroxyl compounds at room temperture. Some of the hydroxyl compounds used were ethanol, $n$-butanol, ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerine, diethylene glycol, dipropylene glycol, and some commercial polyhydroxyl aliphatic compounds. The rate of the reactions was followed by infrared analysis for isocyanate content. The absorbance of the isocyanate peak at 2260 cm$^{-1}$ was measured and compared with the absorbance of a nonchanging peak such as one of those from the methylene groups or the ester groups. From this, the percentage of isocyanate which had reacted at any particular time was calculated. Mixtures containing various catalytic substances were also used to learn their effect on the reaction rate. In addition to infrared analysis, the reaction rate was measured by observing the changing viscosity of the solutions and the time required for gel formation.

## RESULTS AND DISCUSSION

Hundreds of amide-containing resins have been prepared from different combinations of the monomers in the following list: ethyl acrylate, butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, butyl methacrylate, isobutyl methacrylate, styrene, acrylamide, acrylonitrile, methacrylamide, and hydroxypropyl methacrylate. Isocyanate was produced from all of the combinations tried. It has been found that each resin composition requires a different set of reaction conditions for the maximum isocyanate yield. The effect of styrene is particularly significant in increasing the optimum reaction temperature and the amount of hypochlorite required. The methacrylamide–

butylacrylate copolymer described above gave its best yield at near 6°C with 1 mole hypochlorite per mole amide, whereas the methacrylamide–styrene–ethylacrylate polymer gave the best yield at 30°C with 1.5 mole hypochlorite per mole amide.

The tertiary-carbon isocyanates, like most other isocyanates, were found to react very rapidly and completely with primary and secondary amines. The rate was too fast for most practical uses. Diluting some of the less reactive amines with ketone solvents such as methyl ethyl ketone gave slower and useful curing rates. Other amines were converted to imines by reaction with various ketone compounds. In this form, the amines gave useful curing rates.

The "tertiary carbon" isocyanates, like many other isocyanates, were found to react very slowly with hydroxyl compounds in the absence of a catalyst. When mixed with compounds such as ethanol, butanol, or 1,4-butanediol, only a few per cent of the isocyanate reacted after standing for three or four days. In a general way, these isocyanates appear to respond to the usual isocyanate catalysts in the same order as conventional isocyanates. The tin compounds such as dibutyltin diacetate and dibutyltin dilaurate are highly effective catalysts. Tertiary amines are also effective catalysts, but are much slower than the tin compounds. Trace amounts of these catalysts such as are used with other isocyanates have little effect on these tertiary-carbon isocyanates. Catalyst amounts in the range of 2–5% are needed. It has been established that the isocyanate resins as presently prepared contain an inhibitor, and the large quantities of catalyst are required to overcome the effect of the inhibitor. It is expected that the inhibitor will be identified and removed. Useful coating systems have been developed utilizing hydroxy-functional esters cured with tin catalysts.

The isocyanate–hydroxy reaction may be greatly accelerated by mild heating. The data in Table I are from a mixture of lauryl alcohol (2-OH/NCO), 2% dibutyltin dilaurate, and a typical tertiary-carbon isocyanate resin.

Alkali metal hydroxides are potent catalysts for the hydroxyl–isocyanate reaction. They are effective in aqueous solutions, but for polymer curing it is preferred to dissolve them in glycols or polyols. Saturated solutions of lithium hydroxide, sodium hydroxide, and potassium hydroxide in ethylene glycol, diethylene glycol, and glycerine have been evaluated. Lithium hydroxide in ethylene glycol, diethylene glycol, and potassium hydroxide in glycerine appeared to be especially effective in crosslinking the isocyanate resins.

A molar excess of diethylene glycol was mixed with the butyl acrylate–isocyanate resin prepared above. After 15 days (24°C), 30% of the isocyanate had reacted. Lithium hydroxide was added in small increments to other samples of the mixture. Only small increases in reaction rate were seen until the amount of lithium hydroxide exceeded the acid equivalent of the resin. At this point, the reaction became very fast, showing 30% reaction in 15 min. It set to a firm, rubber-like gel a few minutes later. Since other strong bases have a similar effect,

TABLE I
Reaction of an Isocyanate Resin

| Time, hr | Temperature, °C | —NCO, % reacted |
|----------|-----------------|-----------------|
| 1.25     | 24              | 4.12            |
| 1.60     | 100             | 99.50           |

the catalysis appears to result from basicity rather than from a specific metal ion. More specifically, it is believed that the alkoxide ion ($R$—$CH_2$—$O^-$) is the fast-reacting species. Tertiary-carbon isocyanates were mixed with a large variety of substances. In all cases where there was the probability of forming soluble alkoxide ions, reaction was fast; otherwise, it was slow or nil.

Since these reactions were followed by the loss of isocyanate, one might question whether or not the loss resulted from reaction with glycols or polyols. Other reactions are possible. Reaction with glycols is indicated by the formation of stiff gels which do not soften or melt on heating, and the urethane bands are clearly seen in the infrared spectra of the reaction products. Thus, these isocyanates appear to have a greater reactivity toward alcohols and glycols than toward other possible reactants in the reaction mixtures.

Diisocyanate compounds have large and important uses in industry, but most are highly toxic and dangerous to handle. The polymeric isocyanates described here may serve the same uses, but largely avoid these problems. With monomeric isocyanates, much of their hazard results from vaporization. With the isocyanates described here, there seems to be little possibility of vaporization since the amide and isocyanate groups are attached to the polymer chain.

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