

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Modification of Polymers Using Iodine ISocyanate. I. Addition of Iodine ISocyanate to Polyisoprene

Charles G. Gebelein^a

^a Department of Chemistry, Youngstown State University Youngstown, Ohio

To cite this Article Gebelein, Charles G.(1971) 'Modification of Polymers Using Iodine ISocyanate. I. Addition of Iodine ISocyanate to Polyisoprene', *Journal of Macromolecular Science, Part A*, 5: 2, 433 – 442

To link to this Article: DOI: 10.1080/00222337108069389

URL: <http://dx.doi.org/10.1080/00222337108069389>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Modification of Polymers Using Iodine Isocyanate. I. Addition of Iodine Isocyanate to Polyisoprene

CHARLES G. GEBELEIN

*Department of Chemistry
Youngstown State University
Youngstown, Ohio 44503*

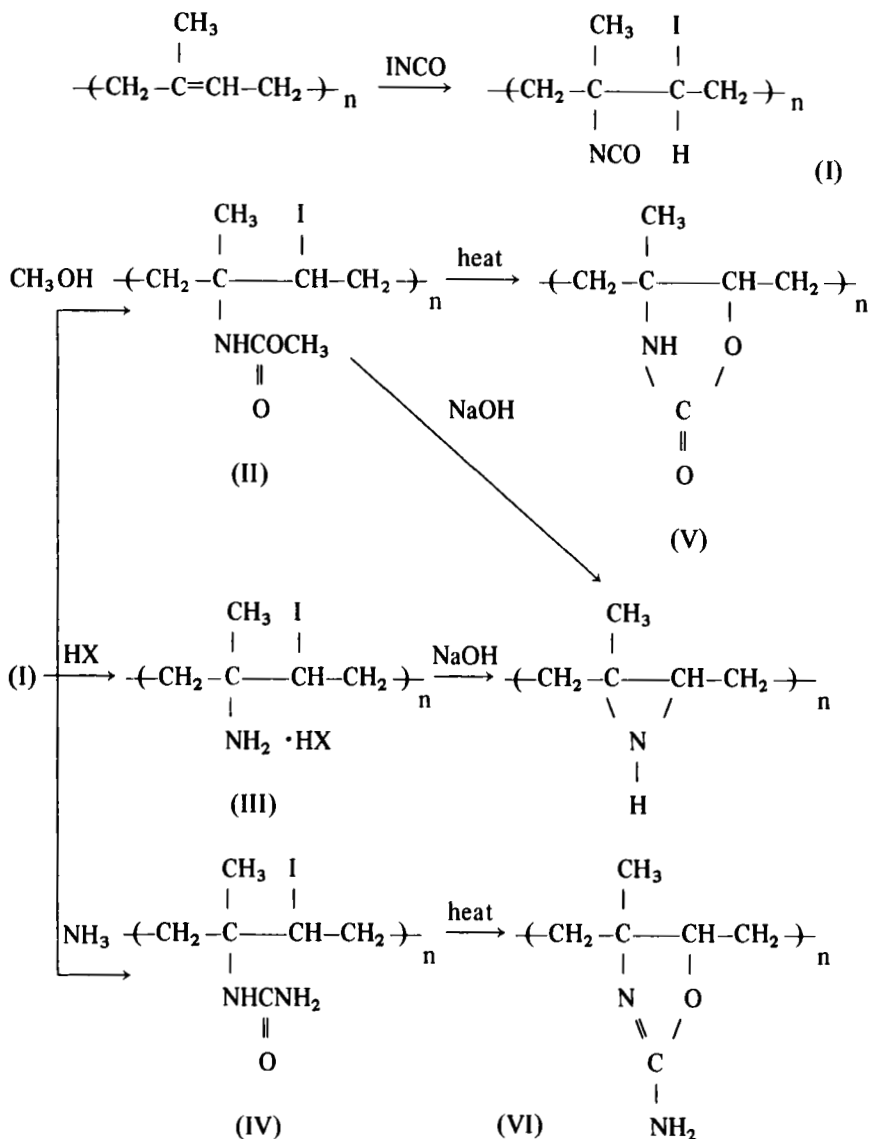
SUMMARY

Iodine isocyanate was added to polyisoprene and converted to the methyl iodocarbamate derivative and the iodourea derivative. The thermal stability of these modified polymers was compared to polyisoprene using simultaneously run thermogravimetric analysis and differential thermal analysis. Both modifications showed initial weight losses starting at about 125°C which correspond to cyclization reactions. Beyond 350°C, the iodourea derivative showed greater thermal stability than the polyisoprene or the methyl iodocarbamate derivative. This enhanced thermal stability is believed due to the formation of a semi-ladder polymer structure.

INTRODUCTION

The modification of unsaturated polymers by chemical reactions such as halogenation, hydrogenation, epoxidation, cyclization, isomerization, and the addition of thiols has been known for many years [1, 2]. Some recent workers have considered the addition of dichlorocarbene and 4-isocyanatophenyl-sulfonyl-chloride [4] to unsaturated polymers. The pseudohalogen iodine isocyanate (INCO) is known to react with a wide variety of unsaturated compounds [5-9], but this reaction has not been

examined with polymeric materials. The addition of iodine isocyanate to unsaturated polymers would provide a route for the introduction of a wide variety of polar, nitrogen-containing functional groups to the polymer backbone. These groups include carbamates, ureas, amines, aziridines, oxazolidones, and oxazoles. These reactions are illustrated for polyisoprene.



We have made exploratory studies to determine 1) whether INCO can actually be added to unsaturated polymers and 2) whether the resulting polymers exhibit any unusual thermal characteristics.

EXPERIMENTAL

Materials

The polyisoprene sample used in these studies was obtained from Shell Chemical (Shell Isoprene Rubber 309) and had a *cis*-1,4-content of 91.5% (balance, 1,2-structure) with a molecular weight of about two million. Eastman grade silver cyanate and a resublimed grade of iodine were used in these studies. All other chemicals and solvents were reagent grade or better.

Addition of Iodine Isocyanate to Polyisoprene

In this study, preformed solutions of INCO were mixed with a solution of the polymer. The generation of INCO follows the procedure of Rosen and Swern [8]. Iodine (16.5 g, 0.065 mole) was dissolved in 300 ml tetrahydrofuran and cooled to -30°C . Silver cyanate (20.0 g, 0.130 mole) was added in one portion and the system was stirred mechanically for 2 hr at -30°C . The stirring was stopped and the supernatant liquid was transferred via a Filterstik to a solution of 6.8 g polyisoprene in tetrahydrofuran/benzene (37.5/62.5) at -30°C . The solution was stirred 3 hr to ensure complete addition of the INCO to the polyisoprene. Subsequent elemental analysis showed that 41% of the monomer repeat units reacted to form Structure I.

The above solution was divided into three portions. Portion A was treated with 100 ml methanol for 24 hr at room temperature to convert it to Structure II. The solvents were removed from this solution to give 4.0 g modified polymer (theory, 4.9 g). The polymer was soluble in the reaction mixture, and slightly soluble in methanol, diethyl ether, tetrahydrofuran, and dimethyl sulfoxide. It was insoluble in benzene, petroleum ether, chloroform, methylene chloride, and acetic acid.

Portion B was treated with 20 ml concd aqueous ammonia for 24 hr at room temperature to convert it to Structure IV. Initially, the reaction solution gelled but complete solution occurred overnight. The solvents were removed under vacuum to give 3.3 g modified polymer (theory, 4.7 g). The polymer did not appear to be completely soluble in any common solvent although it was soluble in the reaction mixture.

Portion C was treated with 20 ml concd aqueous hydrochloric acid and the entire rubber sample coagulated. Complete reaction to Structure III was not achieved in this case and the polymer was not studied further.

Physical Tests

Infrared spectra were obtained on solid films of polyisoprene and the modified polymers using a Perkin Elmer Infracord Model 137. Some selected spectra were also run on a Beckman IR-5.

Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were run simultaneously on a Mettler Thermoanalyzer 2 in aluminum crucibles using 6 liter/hr air flow atmosphere, 10 mg sample, 10°C/min temperature rise, and alumina references. The thermal analyses were run from ambient to 600°C.

Polymer Composition

Elemental analyses of the polymers were used to determine the extent of addition in each polymer studied. The analyses were run by Crobaugh Laboratories.

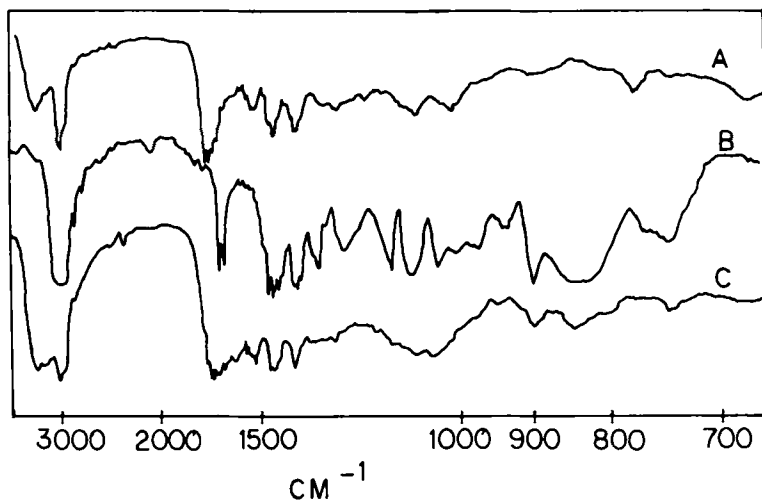


Fig. 1. Infrared spectra for solid films of the methyl iodocarbamate derivative of polyisoprene (A), polyisoprene (B), and the iodourea derivative of polyisoprene (C).

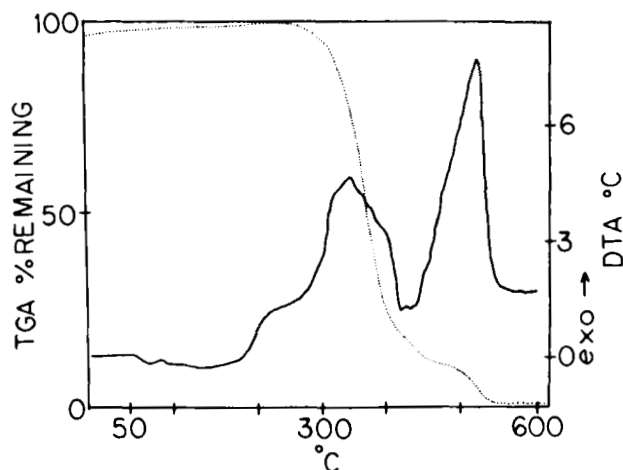


Fig. 2. Thermogravimetric analysis (···) and differential thermal analysis (—) curves for polyisoprene.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra for polyisoprene and modifications of Types II (carbamate) and IV (urea) where INCO has been added to 41% of the double bonds followed by subsequent chemical conversion to the final modification. These spectra are consistent with the proposed structures. The bonds due to unsaturation were reduced, adsorption bands due to OH and NH_2 groups appear at 3400 and 3350, and bands due to $\text{C}=\text{O}$ appear at 1710 and 1740 for Types II and IV, respectively. These spectral assignments are in accord with the literature values for derivatives of simple alkenes [7, 9].

Physically, these modified polymers bear little resemblance to the starting polyisoprene. Both Types II and IV were orange-brown, brittle materials. The three materials differ significantly in thermal stability. Simultaneously determined TGA-DTA curves are shown in Figs. 2, 3, and 4 for polyisoprene, the iodocarbamate derivative (Type II), and the iodourea derivative (Type IV), respectively. Figure 5 compares the TGA curves of all three samples.

Polyisoprene, Fig. 2, showed a rapid weight loss beginning at about 275°C, and this was accompanied by a DTA exotherm which shows a maximum at 350°C. Approximately 50% of the material was lost by 375°C.

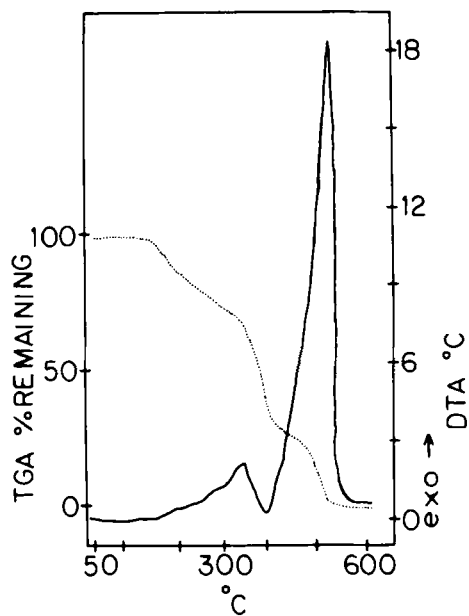


Fig. 3. Thermogravimetric analysis (···) and differential thermal analysis (—) curves for the methyl iodocarbamate derivative of polyisoprene.

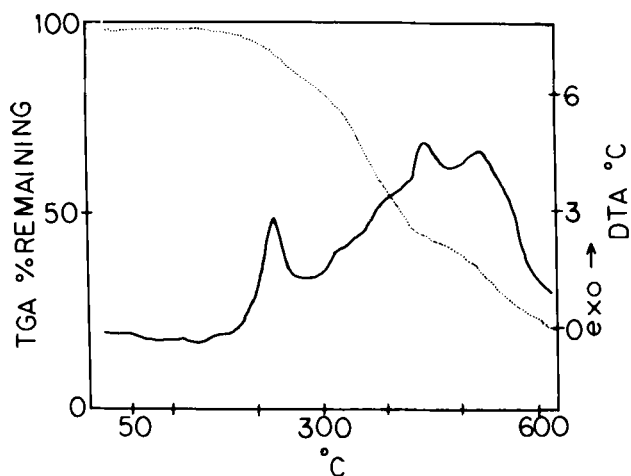


Fig. 4. Thermogravimetric analysis (···) and differential thermal analysis (—) curves for the iodourea derivative of polyisoprene.

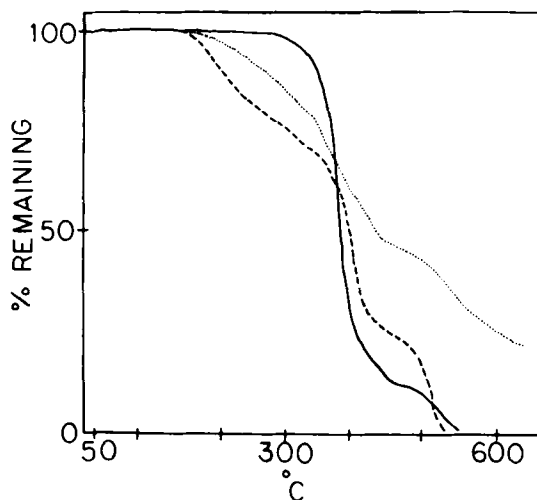


Fig. 5. Comparison of the thermogravimetric curves for polyisoprene (—), the methyl iodocarbamate derivative (---), and the iodourea derivative (···).

A second, more massive, exotherm occurred at 530° , corresponding to the final oxidative degradation of the last 15% of the polymer. The TGA shown here is in good agreement with literature results on natural rubber [10].

The thermal degradation of the iodocarbamate derivative, Fig. 3, is more complex. The initial weight loss began at about 125°C and was slightly exothermic. Approximately 30-35% of the weight was lost gradually up to 350°C where a moderate exotherm occurred followed by a rapid weight loss to a total of about 75%. The remaining 25% weight loss occurs at about 500°C and is accompanied by a massive exotherm. The first weight loss probably corresponds to a ring closure with the elimination of methyl iodide to form structure Type V. This ring closure is known to be facile at moderate temperatures for low molecular weight iodocarbamates [11]. The conversion of the polymer with 41% Type II repeat units to the Type V structure would result in a weight loss of approximately 35%, which is in agreement with the observed weight loss. Structure Type V is a semi-ladder polymer, and some thermal stability enhancement might be expected. The massive exothermic reaction at about 500° may be indicative of enhanced thermal stability. Above 375° , the degradation is slightly slower than that of polyisoprene.

Figure 4 shows the DTA-TGA curves for the iodourea derivative. Like the iodocarbamate, a weight loss begins at about 125°C and was associated

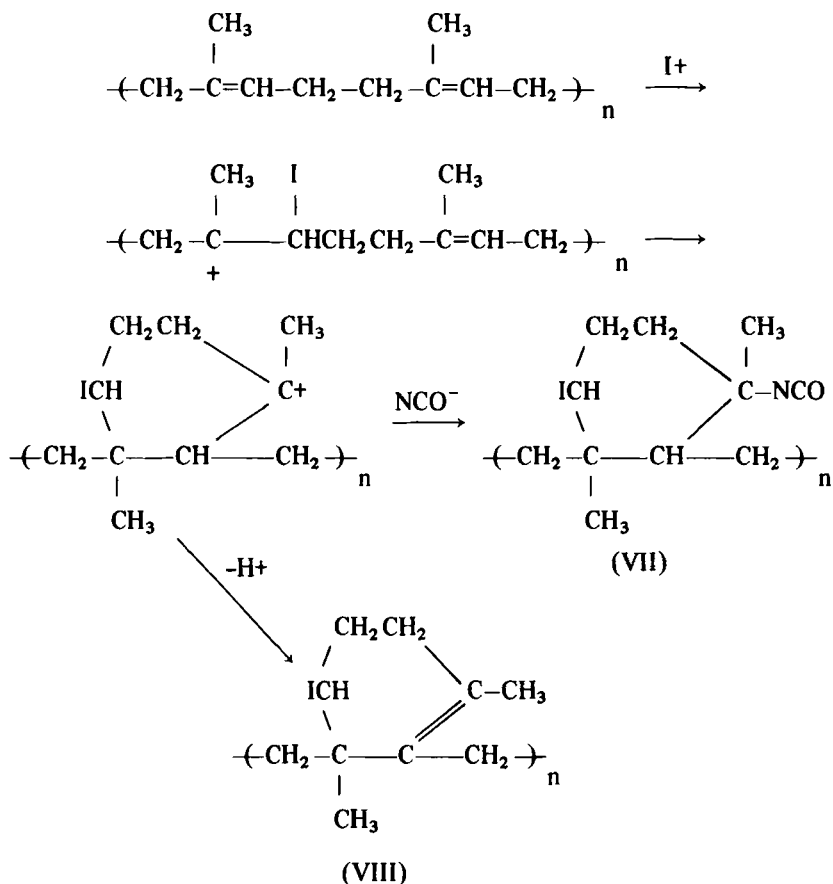
with a mild exotherm in the DTA. A substantial exotherm occurred at about 218°, and this was followed by a series of at least four exotherms with the last one occurring at about 515°C. During this period the sample showed a continuous weight loss but the entire sample did not degrade completely. At 600°C approximately 28% of the polymer remained. The initial weight loss is probably due to the cyclization of structure Type IV to Type VI with the loss of hydrogen iodide. This reaction is known to occur at moderate temperatures [5, 12], and in the case shown here would lead to a weight loss of approximately 35%. The resulting semiladder structure might be expected to show greater thermal stability than polyisoprene.

Figure 5 compares the TGA curves for the initial polyisoprene and the two modifications studied. It is apparent that both derivatives are less stable than polyisoprene below 350° due to an internal cyclization reaction. Above this temperature the iodocarbamate does not show any appreciable improvement in thermal stability compared to the parent polymer but the iodourea is more stable. The most probable explanation for this increase in thermal stability is due to the formation of a semiladder oxazole structure Type VI. Alternate possibilities include cross-linking and other cyclization reactions. The oxidative degradation of polyisoprene is a complex process and can produce cross-linking [13, 14]. However, under the thermal analysis conditions used here, chain scission should be the major reaction for the polyisoprene. The presence of iodine on the polymer backbone in Structures II and IV could lead to increased cross-linking, but the TGA data is more consistent with the cyclization reactions to the iodine-free Structures V and VI. At the present time it is not possible to determine whether Structures V and/or VI would tend to cross-link to a greater extent than does polyisoprene.

Polyisoprene is known to undergo chemical cyclization reactions and such processes are conceivable during the addition of iodine isocyanate. In its simplest form (monocyclic system) this possible side reaction can be written as shown.

Both Structures VII and VIII would be semiladder polymers and could lead to enhanced thermal stability compared to polyisoprene. Each structure contains an iodine atom bound to a six-membered ring. Iodocyclohexane shows C—I stretching bands at 642-657 cm^{-1} [15]. Since no IR adsorption peaks were observed in this region, the presence of Structures VII and VIII is unlikely. In addition, neither structure would account for the low temperature weight losses observed with the iodocarbamate and iodourea derivatives.

The most reasonable explanation for the greater high temperature thermal stability of the iodourea derivative of polyisoprene appears to be the



formation of the semiladder polymer Structure VI. Further studies are planned on this semiladder polymer.

ACKNOWLEDGMENT

This work was partially supported by a grant from the Youngstown State University Research Council. We wish to thank Mr. John Cannon, Mettler Instrument Corp., for running the thermal analyses.

REFERENCES

- [1] E. M. Fettes, ed., *Chemical Reactions of Polymers*, Wiley (Interscience), New York, 1964, Chapter 2.
- [2] K. Meyersen and J. Y. C. Wang, *J. Polym. Sci., Part A-1*, **5**, 725 (1967).
- [3] W. G. DeWitt, III, M. J. Hurwitz, and F. Albright, *J. Polym. Sci., Part A-1*, **7**, 2453 (1969).
- [4] H. Holtschmidt and G. Oertel, *Angew. Makromol. Chem.*, **9**, 1 (1969).
- [5] L. Birckenbach and M. Linhard, *Ber.*, **63**, 2544 (1930); **64**, 961, 1076 (1931).
- [6] G. Drefahl and K. Ponsold, *Chem. Ber.*, **93**, 519 (1960); G. Drefahl, K. Ponsold, and G. Kollner, *J. Prakt. Chem.*, **23**, 136 (1964).
- [7] A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967); A. Hassner, R. P. Hoblitt, C. Heathcock, J. E. Kropp and M. Lorber, *J. Amer. Chem. Soc.*, **92**, 1326 (1970), and references cited therein.
- [8] S. Rosen and D. Swern, *Anal. Chem.*, **38**, 1392 (1966).
- [9] C. G. Gebelein and D. Swern, *J. Org. Chem.*, **33**, 2758 (1968); C. G. Gebelein, S. Rosen, and D. Swern, *J. Org. Chem.*, **34**, 1677 (1969), and references cited therein.
- [10] J. J. Maurer, *Rubber Chem. Technol.*, **42**, 110 (1969).
- [11] T. A. Foglia and D. Swern, *J. Org. Chem.*, **34**, 1680 (1969).
- [12] R. R. Wittekind, J. D. Rosenau, and G. I. Poos, *J. Amer. Chem. Soc.*, **26**, 444 (1961).
- [13] J. I. Cunneen, *Rubber Chem. Technol.*, **41**, 182 (1968).
- [14] P. M. Norling, T. C. P. Lee, and A. V. Tobolsky, *Rubber Chem. Technol.*, **38**, 1198 (1965).
- [15] P. Klæboe, *Acta Chem. Scand.*, **23**, 2641 (1969).

Accepted by editor August 12, 1970

Received for publication August 14, 1970