On Polyalkylidenes

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Riassunto

Vengono riportati gli studi attualmente in corso presso l'Istituto Chimico dell'Università di Torino sulla decomposizione dei diazoalcani per produrre i polialchilideni, polimeri caratterizzati da una sequenza di atomi di carbonio terziario nella catena macromolecolare. Tale reazione di polimerizzazione può venire catalizzata da acidi di Lewis, oppure da metalli pesanti o da loro sali.

L'azione dei metalli, prima di queste ricerche, era limitata essentialmente al rame: gli studi eseguiti particolarmente in questo campo presso l'Istituto Chimico dell'Università di Torino, hanno portato ad una serie di esperienze circa l'azione dei metalli puri sulla reazione catalitica di preparazione di poliidrocarburi a partire dai diazoalcani. L'oro, in particolare, ha fornito, nel caso del diazoetano, un polimero (il polietilidene) altamente cristallino oltre a quello atattico, e così pure si sono ottenuti polimeri cristallini dal diazopropano e dal diazobutano.

Questi studi permettono di proporre, sulla base dei fatti sperimentali, uno schema per la reazione di formazione di polimeri dalla decomposizione dei diazoidrocarburi catalizzata da metalli e per l'azione stereoregolatrice di una superficie metallica.

The interest in studying the formation of the polyalkylidene chain is related to the fact that polymers are obtained the backbone of which is a sequence of tertiary carbon atoms, $(-CHR-)_n$, without the presence of any intermediate $-CH_2-$ groups, as in the case of the polymers of the vinyl or vinylidene types.

Although not directly on the subject of this Conference on polyaddition reactions, the pathway of formation of polyalkylidenes from diazoalkanes, following our mechanism of intermediate carbenes (:CHR), seems not to be a reaction of the vinyl type polymerization, because there is no splitting of the double bond to create the polymer molecule, it is certainly not of the polycondensation type, but is rather related to the polyaddition type. This may be considered as the reason why the paper is presented at this Symposium on polyaddition products.

It would be very interesting, if possible, to get the polyalkylidene chain, of polyethylidene for instance, from a vinyl type polymerization starting from but-2-ene. Until the present time this has not been done, and it would be a very elegant reaction. It is easy to have the reverse reaction, namely to start from the two pieces of but-2-ene (the $:CHCH_3$ carbene) and to join them together to get a dimerization, leading to but-2-ene. This reaction is quite easy, as shown by our experi-

ments. It is also easy to go from the dimerization to the polymerization of the $:CHCH_3$ carbene.

Although it is difficult to open an internal double bond, recent successful experiments with compounds having an internal double bond, such as maleic anhydride[1] and maleinimide,[2] show that the polymerization is, nevertheless, possible. Another remarkable experiment is the stereospecific copolymerization of ethylene with *cis*-but-2-ene to form stereoregular crystalline copolymers.[3] The *cis*-but-2-ene-ethylene copolymer shows that the opening of the internal double bond of *cis*-but-2-ene is possible, at least, when alternating with ethylene.

We will not discuss in detail all the possible mechanisms involved in opening an internal double bond, but we want to stress that the possibility of doing this, using proper energetic and steric conditions does exist.

Until the present, the easiest way to get polyalkylidenes has been to prepare them by catalytical decomposition of diazoalkanes. It is known that diazoalkanes, in the presence of boron compounds such as boron trifluoride, boron alkyls and the esters of boric acid,[4] or of some copper derivatives such as copper stearate,[5] decompose and form polyalkylidenes. Boron compounds are very active catalysts in giving polymethylene from diazomethane but their catalytic activity towards polyalkylidene formation decreases with higher diazoalkanes such as diazoethane, diazopropane, and so on.[6] On the other hand, copper derivatives are much more efficient catalysts in giving polymers from the decomposition products of the higher diazoalkanes than from diazomethane.[6, 7]

Some years ago, being interested in the properties of polymers having side chains, we began to prepare them by catalytical decomposition of diazoalkanes, meanwhile looking for an efficient catalyst. It was thought that $AuCl_3$, being a Lewis acid as well as boron trifluoride, and being the salt of a heavy metal belonging to the same subgroup as copper in the periodic system, might be a suitable catalyst for obtaining polyalkylidenes from the decomposition of diazolalkanes.

Our first experiments[8] confirmed this hypothesis: $AuCl_3$, in the presence of an ethereal solution of diazomethane, was reduced immediately to a red gold colloid and polymethylene occluding colloidal gold was obtained in nearly quantitative yield. The most interesting result arose from the $AuCl_3$ catalyzed decomposition of diazoethane, diazopropane and diazobutane. The behaviour of these diazoalkanes was, generally speaking, similar to the one of diazomethane: $AuCl_3$ was reduced to colloidal gold, but the reaction was not as fast as in the case of diazomethane, polyalkylidenes were formed but the yields were lower than with diazomethane (about 35% of polyethylidene from diazoethane and about 10% of polypropylidene and polybutylidene from diazopropane and diazobutane respectively). The particular point of interest was that, in addition to the amorphous polymers soluble in cold solvents, highly crystalline polyalkylidenes, insoluble in cold solvents, were obtained. The yield of crystalline polyalkylidenes obtained in such a way was about 5% for crystalline polyethylidene and about 2% for crystalline polypropylidene and polybutylidene respectively.[8, 9]

A thorough investigation of the reaction of polyalkylidene formation from the $AuCl_3$ catalyzed decomposition of diazoalkanes led to the conclusion that the catalyst was not the gold salt itself, but the colloidal gold formed from the reduction of $AuCl_3$. The arguments which support this conclusion are:

(1) Polymethylene occluding colloidal gold (the polymer acts as a protective agent of the colloid) decomposes a fresh solution of diazomethane: polymethylene is formed in nearly quantitative yields, and the rate of the reaction does not appreciably differ from that observed if the experiment is performed using the corresponding amounts of $AuCl_3$ and diazomethane.[10] The same results occur when crystalline polyethylidene, polypropylidene or polybutylidene occluding colloidal gold are put in contact with a fresh solution of the corresponding diazoalkane.[8, 9, 10]

(2) Gold hydrosols, prepared according to TURKEVICH[11] by reducing $HAuCl_4$ in aqueous solution with sodium citrate, decompose diazomethane, and diazoethane as well.[12] If the reaction is carried out on a holder for electron microscopy, one observes that after a few minutes the gold particles are sourrounded with a layer of polymer which becomes thicker if the diazoalkanes are allowed to react for a longer time.

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(3) If an ethereal solution of diazomethane is put in contact with a gold film prepared by evaporating gold metal under high vacuum, the diazoalkane decomposes and polymethylene is formed in nearly quantitative yield. The same result occurs with diazoethane, and both amorphous and crystalline polyethylidene are formed.[9,12,13]

In addition to gold, other evaporated metal films have been found to be suitable catalysts for polyalkylidene formation from the decomposition products of diazoalkanes. Some metals, however, are only active in decomposing the diazoalkanes, without any polymer formation.[12,13] Among the metals catalytically active in giving polyethylidene from the decomposition of diazoethane in ethereal solution, copper is to be prominently mentioned. This metal gives practically quantitative yields of the polymer. Among those metals which decompose diazoethane in ethereal solution without polymer formation, we would mention silver.

An investigation on the action of metallic surfaces upon polymer formation from the decomposition products of diazoethane showed that the metals which do not catalyze any polymer formation, although diazoethane is decomposed in a relatively short time, are the transition metals belonging to the second long period of the periodic system and those immediately following them, such as silver. No correlation however can be found between electronic and geometric factors of the metals and their polymer forming capacity. Among those metals which catalyze polymer formation from the decomposition products of diazoethane, only gold is endowed with a stereoregulating activity and gives rise to crystalline polyalkylidenes.

The gas chromatographic analyses of the products formed in addition to polyethylidene and nitrogen in the metal catalyzed decomposition of diazoethane in ethereal solution showed that they are chiefly ethylene, *cis*-but-2-ene and *trans*-but-2-ene, and that the relative amounts of these light hydrocarbons depend upon the capacity of the metal surface to give polymer.[14] The light hydrocarbons evolved during the decomposition of an ethereal solution of diazoethane catalyzed by metals, such as copper and gold, which are active towards polymer formation, are essentially a mixture of nearly equal parts of *trans*-but-2-ene and *cis*-but-2-ene. These arise, of course, from coupling of two ethylidene fragments. When the decomposition of diazoethane in ethereal solution occurs without polymer formation, ethylene represents the main fraction of the light hydrocarbon formed. This is the result of the isomerization of the ethylidene fragment arising from diazoethane.

The crystallinity in polyalkylidenes is, of course, to be attributed to a regular steric arrangement of the side alkyl groups bound to every one of the tertiary carbon atoms which constitute the backbone of the polymer chain. The crystal structure of the polyalkylidenes we prepared is still under investigation. It is rendered difficult by the fact that, up to the present time, it has not been possible to obtain completely oriented fibres of the polymers, probably because of their low molecular weights. The results so far obtained from the study of the electron diffraction spectra of polyethylidene seem to be in agreement with the model of a syndiotactic chain fully extended in the plane.[9]

The infrared spectra of both amorphous and crystalline polyalkylidenes prepared by the metal catalyzed decomposition of diazoalkanes show absorption bands due to the presence of unsaturated groups of the vinyl type in the polymer chain.[9] It is worthy of note that the relative intensity of these absorption bands depends upon the metal used as a catalyst. In this case too, no correlation seems to exist with the metal properties.

On the basis of the main experimental evidence reported here some working hypotheses can be drawn about the path of the reaction leading to polyalkylidene formation from the metal catalyzed decomposition of diazoalkanes. It is reasonable to assume that the first step of the reaction may be the decomposition of the diazoalkane molecules reaching the active sites of the metal surface with subsequent formation of active carbenes, which can be held on the metal surface. These active carbenes then can isomerize, dimerize and polymerize, depending upon the metal surface used as a catalyst. A mechanism of polymerization involving a two-sites attachment on the metal surface during the growth of the polyalkylidene chain might explain the formation of stereoregular polyalkylidenes, when metals having the proper geometric and electronic factors are used as catalysts. The results of our investigations suggest that the limits are very critical, as shown by the fact that, up to the present time, gold only has been found to possess a stereoregulating catalytic activity in the course of the growth of the polyalkylidene chain.

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