

POLYMERS FROM DIAZOALKANES

by

Luigi Trossarelli

Istituto Chimico dell' Universita

Torino (Italy)

The aim of this paper is to describe the work done up to the present time in the Chemistry Department of the University of Torino on the preparation of polyalkylidenes from the catalytical decomposition of diazoalkanes. The interest of this research chiefly lies in the peculiar polyalkylidene chain which is constituted by a sequence of tertiary carbon atoms without any intermediate $-CH_2-$ group, as in the case of the polymers obtained by polymerization of monomers of the vinyl or vinylidene types.

Some kinds of polyalkylidenes have been recently obtained from the polymerization of monomers having an internal double bond such as maleic anhydride (1) and maleinimide (2). Worth of mention is also the stereospecific copolymerization of ethylene with cis-but-2-ene to form stereoregular crystalline copolymers (3).

Up to the present time, however, the easiest way to get polyalkylidenes is to prepare them from the catalytical decomposition of diazoalkanes. It is well known that diazoalkanes, in the presence of boron compounds, such as boron trifluoride, boron alkyls and the ester of boric acid (4), or of some copper derivatives, such as copper stearate (5), decompose diazoalkanes and form polyalkylidenes. It is to be pointed out that 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 started to prepare them from the catalytical decomposition of diazoalkanes, looking at the same time for an efficient catalyst. It was thought that $AuCl_3$, being a Lewis acid as well as boron trifluoride, and the salt of a heavy metal belonging to the same subgroup of copper in the periodic system, could be a suitable catalyst for obtaining polyalkylidenes from the decomposition of diazoalkanes.

Our first experiments (8) confirmed this hypothesis: $AuCl_3$, in the presence of an ethereal solution of diazomethane was reduced as soon to a red gold colloid and polymethylene occluding colloidal gold was obtained with nearly quantitative yield. But 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; the 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) and, this is the point of interest, in addition to the amorphous polymers, soluble in cold solvents, highly crystalline polyalkylidenes, insoluble in cold solvents, were obtained. The yields of crystalline polyalkylidenes obtained in such a way were 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 lead 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 amount of AuCl_3 and diazomethane (10). The same happens 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, it is easy to observe that, after a few minutes, the gold particles are surrounded with a layer of polymer, which becomes thicker if the diazoalkanes have been allowed to react for a longer time;
- (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 happens with diazoethane, and both amorphous and crystalline polyethylidene are formed (9, 12, 13).

In addition to gold, many other metals, as evaporated metal films, have been found to be suitable catalysts for polyethylidene formation from the decomposition products of diazoethane, while some other metals are only active in decomposing diazoethane, but 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 remembered, which gives practically quantitative yield of the polymer, and among those metals which only decompose diazoethane in ethereal solution without polymer formation, we

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

The gaschromatographic analysis of the products formed, besides 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 relative amount of these light hydrocarbons depends upon the ability of the metal surface to give polymer or not (14). As a matter of fact, the light hydrocarbons evolved during the decomposition of an ethereal solution of diazoethane catalyzed by metals active towards polymer formation, such as copper and gold, are essentially a mixture in nearly equal parts of trans-but-2-ene and cis-but-2-ene, which of course, arise 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, as 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, and it is rendered difficult by the fact that, up to the present time, it has not been possible to obtain completely oriented fibers of the polymers, much probably because of their low molecular weights. The results so far obtained on polyethylidene from the study of the electron diffraction spectra 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 band due to the presence of unsaturations of the vinyl type in the polymer chain (9). It is worth of note the fact that the relative intensity of the absorption bands due to unsaturations of the vinyl type in the polymer molecule, depends upon the metal used as a catalyst, but in this case too, no correlations seem to exist with the metal properties.

On the basis of the main experimental evidences reported here, some working hypotheses can be drawn about the path of the reaction leading to polyalkylidenes from the metal catalyzed decomposition of diazoalkanes. It is reasonable to assume that the first step of the reaction might be the decomposition of the diazoalkane molecules reaching the active sites of the metal surface, with nitrogen liberation and consequent formation of active carbenes, which can be held on the metal surface. These active carbene can then 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 probably explain the formation of stereoregular polyalkylidenes, when metals having the proper geometric and electronic factors are used as catalysts. From the results of our investigation it seems that the limits are very critical, as shown by the fact that gold only, up to the present time, has been found to possess a stereoregulating catalytic activity in the course of the growth of the polyalkylidene chain.

References

1. Chem. & Eng. News, Sept. 11, 1961, Pag. 52.
2. P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, R. Williams, J. Org. Chem., 26, 15 (1961).
3. G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori, A. Zambelli, J. Am. Chem. Soc., 83, 3343 (1961).
4. H. Meerwein, Angew Chem., 60, 78 (1948); A. Ya. Yakubovich, V. A. Ginsburg, Doklady Akad. Nauk USSR, 73, 957 (1950); G. D. Buckley, N. H. Ray J. Chem. Soc., 1952, 3701; S. W. Kantor, R. C. Osthoff, J. Am. Chem. Soc., 75, 931 (1953); J. Feltzin, A. J. Restaino, R. B. Mesrobian, Ibid., 77, 206 (1955); V. V. Korshak, V. A. Sergeev, Doklady Akad. Nauk USSR, 115, 308 (1957); C. E. H. Bawn, A. Ledwith, P. Matthies, J. Polymer Sci. 34, 93 (1959)
5. G. D. Buckley, L. H. Cross, N. H. Ray, J. Chem. Soc., 1950, 2714; C. E. H. Bawn, T. B. Rhodes, Trans. Faraday Soc., 50, 934 (1954); J. Feltzin, A. J. Restaino, R. B. Mesrobian, J. Am. Chem. Soc., 77, 206 (1955); C. E. H. Bawn, A. Ledwith, J. Whittleston, IUPAC-Symposium uber Madromolekule 1959 in Wiesbaden, Short Communications, paper III A 15.
6. J. Feltzin, A. J. Restaino, R. B. Mesrobian, J. Am. Chem. Soc., 77, 206, (1955)
7. G. D. Buckley, L. H. Cross, N. H. Ray, J. Chem. Soc., 1950, 2714.
8. G. Saini, A. G. Nasini, Atti Acc. Science Torino, Classe Sci. Fis. Mat. Nat. 90, 586 (1955-56).
9. A. G. Nasini, L. Trossarelli, G. Saini, Makromol. Chem., 44-46, 550 (1961)
10. G. Saini, E. Campi, S. Parodi, Gazz. Chim. ital., 87, 342 (1957).
11. J. Turkevich, P. C. Stevenson, J. Hillier, Disc. Faraday Soc., 11, 55 (1951)
12. G. Saini, G. Ostacoli, S. Parodi, Chim. e Ind., 40, 467 (1958).
13. L. Trossarelli, E. Campi, A. G. Nasini, IUPAC-Symposium uber Makromolekule 1959 in Wiesbaden, Short-Communications, paper III A 16.
14. A. G. Nasini, G. Saini, L. Trossarelli, E. Campi, J. Polymer Sci., 48, 435 (1960)