Reports of the Academy of Sciences of the USSR

Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK and V. A. SERGEEV

1957

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1957. Volume 115, No. 2

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK and V. A. SERGEEV

ON THE FORMATION OF POLYMERIC HYDROCARBONS DURING THE DECOMPOSITION OF ALIPHATIC DIAZO COMPOUNDS

The decomposition of aliphatic diazo compounds, leading to the formation of polyhydrocarbons (^{1}), has been studied by a number of investigators in the presence of various catalysts ($^{2-11}$).

We have carried out a comparative study of the decomposition reactions of diazomethane, diazoethane, diazotoluene, and diazodiphenylmethane, as well as of their mixtures, in the presence of metallic copper and certain boron compounds (trimethyl borate or boron fluoride).

Fig. 1. Rate of nitrogen evolution with time during the decomposition of diazomethane (1.4 g): 1—in the presence of metallic copper (1 g), 2—in the presence of trimethyl borate (0.3 g). Diazomethane concentration: 0.85 g in 100 ml of solution.

The decomposition of diazomethane in the presence of trimethyl borate is characterized by the presence of an induction period, as can be seen in Fig. 1. In addition, an essential difference in the action of these catalysts consists in the fact that trimethyl borate causes a more rapid decomposition of diazomethane and leads to the quantitative formation of polymethylene $(CH_2)_x$. The gaseous products contain only nitrogen, and hydrocarbons are completely absent. In the case of copper, the yield of polymers is only 10-15%, and the nitrogen contains ethylene; in addition, various nitrogen-containing products are formed. It may be considered that the reaction of polymethylene formation from diazomethane is an ionic process having certain features in common with the polymerization of olefinic hydrocarbons under the influence of ionic catalysts.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Diazoethane also decomposes in the presence of copper, forming the corresponding polymeric hydrocarbon. The yield of polyethylidene is 40%, i.e., higher than in the decomposition of diazomethane.

Diazotoluene in the presence of boron fluoride etherate forms only benzaldehyde azine and evolves nitrogen. We note, incidentally, that the formation of the corresponding azines was also observed by us during the decomposition of diazomethane and diazoethane, but they were obtained only in small quantities.

Diazodiphenylmethane in the presence of boron fluoride forms only benzophenone azine and evolves nitrogen.

We then obtained copolymers—by decomposing mixtures of diazomethane with diazoethane in the presence of trimethyl borate, and of diazomethane with diazotoluene in the presence of boron fluoride. It was found that in this case a mixture of products is formed, consisting of polymethylene, the corresponding copolymer, and a mixture of the corresponding azines.

In the decomposition of a mixture of diazomethane and diazoethane, a copolymer was formed which, depending on the quantitative ratios of the starting ...

···of substances was polymethylene containing different numbers of side methyl groups.

The copolymer obtained may be regarded as an analogue of polyethylene obtained at high pressure, if the number of side methyl groups is small. In the case of equal ratios of the starting substances, the copolymer obtained may be regarded as an analogue of polypropylene.

Figure 2 gives the thermomechanical characteristics of polymethylene obtained in the presence of copper (curve 1), and, for comparison, of low-pressure polyethylene obtained in the presence of triethylaluminum (2).

Fig. 2

Fig. 3

Fig. 1. Deformation of polymers as a function of temperature under the action of a constant load (100 g/4 mm) at a heating rate of 75° per hour

Fig. 2. Deformation of polymers as a function of temperature under the action of a constant load (100 g/4 mm) at a heating rate of 75° per hour

The same figure also gives curves for polyethylene obtained in the presence of copper (3), and high-pressure polyethylene (4).

Fig. 4. Deformation of polymers as a function of temperature under a constant load (100 g/4 mm) at a heating rate of 75° per hour.

Figure 3: Fig. 4. Deformation of polymers as a function of temperature under a constant load (100 g/4 mm) at a heating rate of 75° per hour.

As is seen from Fig. 2, the curves for polymethylene from diazomethane (1) and low-pressure polyethylene (2) practically coincide completely, which indicates their identical structure. The curve for polyethylidene (3) lies considerably to the left and shows a completely different structure of this polymer in comparison with the others. The curve for high-pressure polyethylene (4) occupies an intermediate position, thereby indicating the presence of side groups.

An X-ray diffraction study of polymethylene obtained from diazomethane and of low-pressure polyethylene showed that both are crystalline products with a degree of crystallinity up to 90–100%. In contrast to these products, high-pressure polyethylene proved to be partly amorphous. The X-ray pattern of polyethylidene also indicates partial crystallinity of this polymer, reaching 25%.

Figure 3 gives the thermomechanical curves for copolymers obtained in the presence of copper from diazomethane and diazoethane at different ratios of the latter (1—at 3%; 2 and 3—at 74% diazoethane), and also, for comparison, the curves for polymethylene obtained from diazomethane (4), and polyethylidene obtained from diazoethane (5). As is seen from this figure, the curve for the copolymer obtained with a content of 3% diazoethane shows the onset of softening at the same temperature as in polyethylidene obtained from diazoethane alone (5), and then approaches the curve for polymethylene. This manifests the influence of the existing

methyl groups; however, no similarity to high-pressure polyethylene is observed (see Fig. 2). This can apparently be explained by the fact that high-pressure polyethylene is a polymer having branched macromolecules, whereas our copolymer has only short methyl groups.

Upon decomposition of a mixture of 74 mole % diazoethane and 26 mole % diazomethane, a product is obtained, part of which is soluble in ether. Thermomechanical curves were recorded both for the soluble and for the insoluble part of the copolymer.

Curve 2 (Fig. 3) corresponds to the copolymer obtained at a diazoethane content of 74% and belongs to the part of the product insoluble in ether. This curve, like the curve for the soluble part of the polymer (3) obtained at the same ratios, shows the onset of softening at a lower temperature.

Fig. 4. Deformation of polymers as a function of temperature under a constant load (100 g/4 mm) at a heating rate of 75° per hour.

However, further on the appearance of these curves becomes different: the curve for the soluble copolymer (3) is, in its form, analogous to the curve for polyethylene, differing only in a lower softening temperature. The curve for the insoluble copolymer (2) is generally similar to the curve for the copolymer obtained at 3% diazoethane and ultimately approaches the curve for polymethylene obtained from diazomethane alone.

Figure 4 gives thermomechanical curves for polystyrene (1) obtained by copolymerization of diazomethane and diazotoluene in the presence of boron fluoride, for block polystyrene obtained by radical polymerization of styrene (2), and for polymethylene obtained in the presence of boron fluoride etherate (3). As can be seen from this figure, the polystyrene formed during copolymerization of diazomethane with diazotoluene has a high melting temperature (about 220-224°); moreover, it is insoluble in ether and heptane and resembles "isotactic" polystyrene (12).

The formation of unbranched regular polystyrene under our conditions cannot be associated with the orienting influence of the crystalline surface of the catalyst, as Natta (12) and other investigators (13) suppose. Apparently, the more correct view is that the cause of the regular arrangement of substituents in the molecule of this polystyrene is the regulating influence of side groups in the course of polymer formation. This self-regulation depends primarily on the spatial influence of groups, generally analogous to that observed in the polymerization of vinyl-type monomers. We proposed designating this spatial influence as "stereochemical factors," understanding by this the entire sum of spatial effects that depend primarily on the size of the substituents and are determined by their volume (15-17). These effects were manifested primarily in the polymerization and copolymerization of monomers, and therefore this aspect was previously examined by us in detail on a large number of examples (15). Evidently, it is now necessary to supplement these ideas by taking into account the influence exerted by substituents on the order of combination of units in the polymer macromolecule. When phenyl groups are arranged alternately, as is the case in polystyrene, the addition of each succeeding residue containing a phenyl group can occur only with such an arrangement of the phenyl group in space that there is no po-

···from the side of the already existing phenyl group; it is easy to see that in such a case the phenyl groups will be located on the outer side of the spiral.

The fact that, in the case of radical polymerization, such a regular arrangement of substituents does not occur can be explained by the fact that the free radical which is the terminal carbon atom of the growing macromolecule is a planar formation, and since its transition to a tetrahedral structure is equally probable in both directions, the configuration of the polymer formed represents a case of equiprobable arrangement of substituents in different positions, leading to the absence of regularity in the arrangement of substituents and to the formation of a polymer with a low melting point.

In the case of formation of a copolymer from diazomethane and diazotoluene, we have an ionic process, and this ensures preservation of the same configuration of the carbon atoms in the copolymer formed. In the case of the copolymer from diazomethane and diazoethane, formation of an isotactic copolymer is not observed, evidently because the methyl groups are still not large enough for their interaction to ensure the effect of self-regulation.

Evidence for the presence of steric hindrance may also be seen in the fact that joint decomposition of a mixture of diazomethane and diazodiphenylmethane does not lead to the formation of a copolymer. Only the formation of benzophenone azine and polymethylene is observed.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
15 III 1957

REFERENCES CITED

1. E. Bamberger, F. Tschirner, Ber., **33**, 955 (1900).
2. H. Meerwein, H. Rathjen, Ber., **75**, 1610 (1942).
3. L. Leitch, P. Gagnon, A. Cambron, Can. J. Res., **28B**, 256 (1950).
4. G. Buckley, L. Cross, N. Ray, J. Chem. Soc., 1950, 2714.
5. C. Bawn, T. Rhodes, Trans. Farad. Soc., **50**, 934 (1954).
6. H. Meerwein, Angew. Chem., **60A**, 78 (1948).
7. G. Buckley, N. Ray, J. Chem. Soc., 1952, 3701.
8. I. Kantor, R. Osthoff, J. Am. Chem. Soc., **75**, 931 (1953).
9. K. Hamann, Zs. Elektrochem., **60**, 317 (1956).
10. P. Plesch, Zs. Elektrochem., **60**, 325 (1956).
11. I. Feltzin, A. Restaino, R. Mesrobian, J. Am. Chem. Soc., **77**, 206 (1955).
12. G. Natta, Angew. Chem., **68**, 303 (1956).
13. C. F. Schildknecht, S. T. Cross, H. K. Davidson, I. M. Laubent, Ind. and Eng. Chem., **40**, 2104 (1943).
14. V. V. Korshak, Izv. AN SSSR, OKhN, 1949, 269.

15. V. V. Korshak, *Chemistry of High-Molecular Compounds*, Izd. AN SSSR, 1950, p. 178.
16. V. V. Korshak, N. G. Matveeva, DAN, **85**, 797 (1952).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.