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472

Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band 71

1964

Seite 212-214

Kurzmitteilung

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of β -(N-Carbazyl)-Ethylmethacrylate**

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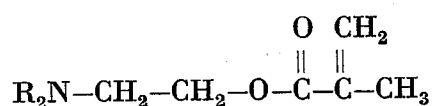
**Anionic Stereospecific Polymerization
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(Eingegangen am 16. November 1963)

Anionic stereospecific polymerization of alkyl acrylates or methacrylates in the presence of organometallic compounds¹⁾ or metalloamide compounds²⁾ was already known.

However, whether high polymers and particularly, crystalline polymers of β -aminoethylmethacrylates corresponding to the general formula



(wherein R can be an alkyl, aryl, cycloalkyl or heterocyclic group) could be obtained by anionic polymerization, was up to now unknown.

We found that, although with the aid of peculiar experimental conditions, β -aminoethylmethacrylates can be polymerized in the presence of some organometallic or metalloamide compounds as catalysts. For instance the anionic polymerization of β -aminoethylmethacrylates can be performed within a temperature range of -80° to $+20^\circ C.$, by using toluene as solvent and *n*-butyl lithium, N-carbazyl lithium, diethylmagnesium (and sometimes phenylmagnesium bromide or diethylaminomagnesium bromide) as catalysts. Anyhow, polymerization rates of β -aminoethylmethacrylates were found always lower (generally corresponding to no more than 10–15% of monomer to polymer conversion, within 20 hrs. of polymerization) than ones observed in the case of anionic polymerization of, e.g., the methylmethacrylate. The obtained poly β -aminoethylmethacrylates are amorphous, not crystallizable (atactic) polymers.

In the case of the β -(N-carbazyl)-ethylmethacrylate polymerization we succeeded in obtaining a linear, head to tail, high molecular weight polymer containing stereoregular macromolecules and showing a high crystallinity by X-rays examination.

Such a crystalline poly β -(N-carbazyl)-ethylmethacrylate was particularly obtained by polymerization in toluene solution at 0–20°C. in the presence of diethylaminomagnesium bromide or phenylmagnesium bromide as a catalyst, after the procedure described in our previous paper²⁾. The crude polymer is generally amorphous and needs an annealing treatment (*i.e.*, refluxing in methylhexylketone or heating at 170 to 190°C. under nitrogen atmosphere for 2–4 hrs.) in order to crystallize. Fig. 1 shows a X-rays diffraction diagram (CuK α , GEIGER registration)

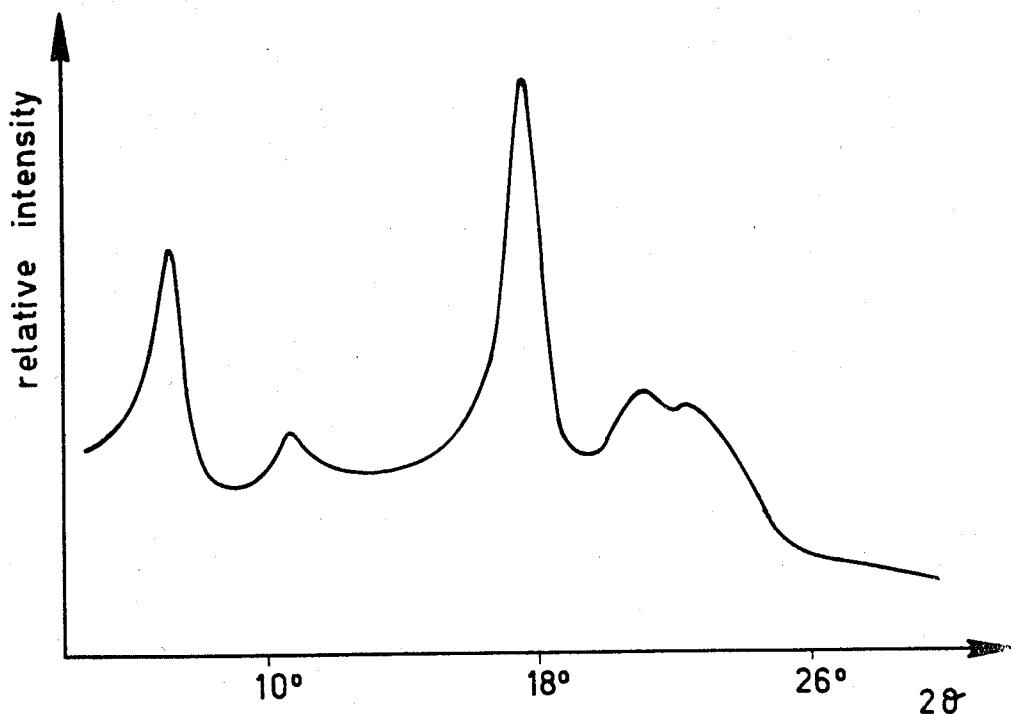


Fig. 1. X rays diffraction diagram (CuK α , GEIGER registration) of the crystalline poly- β -(N-Carbazyl)-ethylmethacrylate

of the crystalline poly β -(N-carbazyl)-ethylmethacrylate. Melting temperature of the crystalline polymer, determined by polarized light microscope (heating rate: 0,5°C./min.), ranges between 280 and 293°C. The crystalline polymer is soluble in hot nitrobenzene and diphenylether, partially soluble in boiling aniline. Intrinsic viscosities in nitrobenzene at 135°C. are generally 0.1–0.3 [100 ccm./g.]. We can attribute the occurrence of a stereospecific polymerization of β -(N-carbazyl)-ethylmethacrylate to the peculiar nature of the nitrogen atom of the carbazyl group; as a matter of fact, this nitrogen atom lacks of nucleophilic character. Therefore, the molecule of β -(N-carbazyl)-ethylmethacrylate contains only oxygen atoms as electron donor atoms, which are able to coordinate with the organometallic or metalloamide catalyst. Formation of stereoregular macromolecules, like in the case of polymethylmethacrylate, can be hence expected.

On the contrary, β -dialkyl- or β -dicycloalkylaminoethylmethacrylates contain both nitrogen and oxygen atoms as electron-donor atoms which are able to coordinate with the catalyst. Such a competitive action should probably trouble the stereoregular growing of the macromolecules, so that crystallizable polymer in this case could not be formed. On the other hand, as a consequence of the formation of very strong coordination complexes of the catalyst with nitrogen atom, low rate of polymerization (according to the obtained experimental data) can be expected.

That coordination between catalyst and β -(N-carbazyl)-ethylmethacrylate is a necessary first reaction step in order to get a stereoregular growing of the macromolecules, is well proved by the fact that radical initiated polymerization produces only amorphous, not crystallizable polymer. This also proves that steric hindrance of the carbazyl group is not an important factor as for the stereoregular growing of the macromolecules. A detailed study of radical initiated polymerization of several β -aminoethylmethacrylates (including the β -(N-carbazyl)-ethylmethacrylate) and a report of some properties of the obtained polymers is now in progress³⁾.

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