Thesis

THE PREPARATION AND PROPERTIES OF STEREOREGULAR POLY (N-SUBSTITUTED ACRYLAMIDES)

A study of the synthesis of the synthesis of poly (N-monosubstituted acrylamides) from stereoregular poly (alkyl acrylates) and an examination of their physical properties, including a comparison with atactic analogues.

N.A-R.Matar, The Preparation and Properties of Stereoregular Poly(N-Substituted Acrylamides), Ph.D. Thesis, University of Bradford, England, U.K. (1983)

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Supervisors: Dr.R.J.Fort and Prof. I.Goodman. External Examiner: Prof. J.McIntyre (Leeds University,U.K.)

ABSTRACT

Poly(acryloyl chloride), prepared by free radical polymerization in solution and presumed to be highly syndiotactic, was reacted with amines to form N-monosubstituted acrylamide polymers. Although some derivatives were unexpectedly crystalline, the polymeric acid chloride was found not to be suitable for the preparation of the stereoregular polyacrylamides.

Since stereoregular polyacrylic and polymethacylic a cids are readily obtained by the hydrolysis of the corresponding polyacrylic esters, these were selected as convenient precursors of the polyacrylamides. Thus, isotactic poly(methacrylic acid) of reasonable molar mass and high steric purity was obtained by acidic hydrolysis of isotactic PMMA.

Atactic and isotactic poly(methacrylic acid)s reacted with more than equimolar amounts of various amines in DMF/pyridine at reflux temperature for 6 hours and in the presence of dicyclohexylcarbodiimide (DCC) as a coupling reagent to give atactic and isotactic N-monosubstituted methacrylamide polymers. Amidation occurred with a substantial degree of conversion but the side-product, 1, 3-dicyclohexylurea, presented a purification problem in some cases. In such cases, the alternative use of a water-soluble carbodiimide or of diphenylcarbodiimide proved to be an adequate solution.

Amidation of low molecular weight model compounds in the presence of DCC, and reactions conducted during the study of the mechanisms of the amidation reaction, indicated that amidation by means of DCC does not proceed through an anhydride intermediate and that the simple organic as well as the polymeric end products are, most probably, free from imide groups.

While the hydrolysis and amidation processes appeared not to affect the stereochemical integrity of the polymer backbone, the low molar masses of the resulting polymethacrylamides and the results of remethylation of the isotactic polyacid gave an indication of some chain degradation during the hydrolysis step.

The stereoregular N-monosubstituted methacrylamide polymers prepared by amidation of hydrolysed poly(methyl methacrylate) (PMMA)contain some residual ester and acid groups. They were found to possess nearly the same physical properties as their atactic analogues except for solubility and film-forming properties. Both types of polymers displayed similar IR and NMR spectra and had poor thermal and mechanical properties. Stereoregular polymethacrylamides seem to have few hydrogen bonds in the solid state and in solution possibly due to the steric effect of the α-methyl groups.

Stereoregular and atactic N-α-methylbenzylmethacrylamide polymers were found to have some helical conformation in solution as indicated by ORD, CD, and U.V. measurements. Surprisingly, the occurrence of a double-helix conformation is possible in both kinds of polymers and while it can be assumed to result from isotactic PMMA in the case of the stereoregular polymer, no explanation can be given for such order in the atactic counterpart.