

Synthesis and Characterisation of Poly(N-4'-Fluorophenylmethacrylamide)

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SUMMARY

The monomer, N-4'-fluorophenylmethacrylamide (FPMA) was polymerized for the first time using benzoyl peroxide as the initiator. The IR and NMR spectra of FPMA and the polymer, poly(N-4'-fluorophenylmethacrylamide) (PPFMA) are discussed. Viscosity measurements of PPFMA was carried out in dimethylformamide medium at 25°C. The number average molecular weight of PPFMA was determined to be 690 using vapour pressure osmometer. The formation of low molecular weight of PPFMA is explained on the basis of intermolecular hydrogen bonding in the monomer.

INTRODUCTION

The N-substituted acryl- and methacrylamides are used as adhesives, fibers, films and flocculants. In copolymers, the methacrylamide with bulky substituents impart stiffness and increase the softening temperature. (THOMAS, 1964). The copolymers of N-phenylmethacrylamide with unsymmetrical dichloroethylene is suitable for producing moulded articles (ARNOLD, 1942), while the copolymers with the high alkyl acrylic esters are used as lubricating-oil additives (CATLIN, 1952). Synthesis of some N-substituted methacrylamides has been reported (KOTON et al., 1957; SOKOLOVA, 1957) and the first synthesis of fluorophenylmethacrylamides was reported by Sokolova and Ovsyannikova (SOKOLOVA and OVSYANNIKOVA, 1958). The copolymerization of N-3'-fluorophenylmethacrylamide with methacrylic acid and its application as antibody resins was reported by MANECKE and SINGER (1960); MANECKE and GUENZEL (1962a); MANECKE (1962b); MANECKE and SINGER (1962c).

By the introduction of a halogen atom especially fluorine in the phenyl ring of N-phenylmethacrylamide, the properties of the polymer may markedly change. With this view, N-4'-fluorophenylmethacrylamide was synthesized and was polymerized using benzoyl peroxide as the catalyst. This is the first report of the polymerization of this monomer.

EXPERIMENTAL

Methacryloyl chloride was prepared from methacrylic acid and thionyl chloride as previously reported (KOTON et al., 1957).

p-fluoronitrobenzene was prepared from p-nitroaniline according to the known procedure (STACY et al., 1965).

p-fluoroaniline was synthesized by a method analogous to that reported (VOGEL, 1975) for the preparation of aniline from nitrobenzene.

N-4'-fluorophenylmethacrylamide was prepared by the method of Sokolova and Ovsyannikova (SOKOLOVA and OVSYANNIKOVA, 1958).

1 g of N-4'-fluorophenylmethacrylamide was dissolved in 5 ml of benzene and deaerated for 30 minutes using pure, dry Nitrogen. To this 30 mg of benzoyl peroxide, dissolved in 5 ml of benzene was added and deaerated for another 10 minutes. The tube was sealed and heated in a bath maintained at 60°C for 18 hrs. Then the polymer solution was concentrated, dissolved in absolute ethanol and poured in water to precipitate the polymer. The polymer was purified by reprecipitation. The polymer was filtered and dried in an oven at 60°C.

The infra-red spectra of the amide and the polymer were recorded in a Beckmann IR-20 spectrometer using KBr disc.

The proton magnetic resonance spectrum was recorded in a Varian XL-100 spectrometer using CDCl₃ and DMSO-d₆ as the solvents for the monomer and the polymer respectively (TMS as the reference).

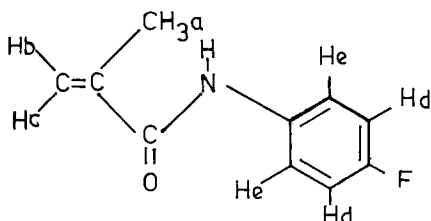
The intrinsic viscosity of the polymer was found in an Ubbelohde viscometer using dimethylformamide as

the solvent.

The molecular weight was determined in the Knauer Vapour pressure osmometer using dimethylformamide as the solvent at 90°C.

RESULTS AND DISCUSSION

The monomer, N-4'-fluorophenylmethacrylamide was synthesized according to the procedure reported. In the IR spectrum recorded, a band at 3260 cm^{-1} showed the presence of a substituted amide group in the monomer whose structure is



The presence of the amide carbonyl group and olefinic group can be seen by the two bands at 1660 cm^{-1} and at 1620 cm^{-1} respectively. The strong absorption at 1400 cm^{-1} shows the presence of fluorine atom in the monomer.

In the NMR spectrum of the monomer, the methyl protons H_a appeared at 1.98ppm. The peaks at 5.40ppm and 5.75ppm were due to the two olefinic protons H_b and H_c . The absorption at 6.96ppm was due to the two H_d protons and peak at 7.50ppm was for the two H_e protons. The $>N-H$ proton appeared at 8.1ppm. The presence of the $>N-H$ proton was further confirmed by deuterium exchange studies using D_2O .

Homopolymerization was carried out in an inert atmosphere using benzoyl peroxide as the catalyst. The polymer got precipitated from benzene solution, the monomer being soluble in benzene.

Further evidence was obtained from the IR and the NMR spectrum of the polymer. The IR spectrum of the polymer was similar to that of the monomer except for the disappearance of the absorption at 1620 cm^{-1} , which confirms polymerization. In the NMR spectrum of PFPMA the $>N-H$ proton appeared at 9.36ppm. The broad peak at 7.34ppm was due to the protons H_d and the

other broad peak at 7.72ppm was for the H_e protons. The methylene protons H_b and H_c appeared at 2.28ppm. The peak at 1.40ppm was due to the methyl protons H_a present in PFPMA. These data revealed that PFPMA had a linear structure.

The intrinsic viscosity $[\eta]$ was found using dimethylformamide as the solvent at $25 \pm 0.1^\circ\text{C}$. The low value 0.022 dl/g suggested that the polymer may be of low molecular weight. A molecular weight of 690 was obtained from vapour pressure osmometry. The molecular weight was also determined by the depression of freezing point method also given a value of 678.

An investigation on the homopolymerization of o-, m- and p-methoxy, ethoxy (SOKOLOVA and OVSYANNIKOVA 1959) and carbethoxy (SOKOLOVA et al., 1959) phenyl-methacrylamides showed that the reactivity of meta and para isomers was less as compared to the ortho isomer due to the presence of intermolecular hydrogen bonding in the m- and p-isomers.

Generally in an IR spectrum, a free N-H group would be indicated by a band at 3430 cm^{-1} . But the absorption at 3260 cm^{-1} of medium intensity in the monomer spectrum shows the presence of hydrogen bonded amide group. So the previous studies (SOKOLOVA and OVSYANNIKOVA, 1959a, SOKOLOVA et al., 1959b, SOKOLOVA et al., 1959c) and the above IR spectral evidence explain that the low molecular weight polymer from FPMA is due to the inter molecular hydrogen bonding in FPMA.

To ascertain this fact, the synthesis and the polymerization of m- and o-isomers of FPMA is under progress.

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