Linde Molecular Sieve 5A which had been evacuated at 10^{-5} mm. and 350° for 15 hours, a type I isotherm was obtained, in which the flat was attained at a low relative pressure (P/P was 0.00506 at 25°). The corresponding adsorption was 0.20 g. sorbate per g. of sorbent. Each point required about 24 hours for equilibration. When desorption was commenced, a large loss of sorbate with decreasing pressure was observed, placing the desorption isotherm below the adsorption isotherm, rather than above it, the latter normally being expected. Considerable divergence of the two curves was seen down to a pressure of approximately 20 mm. Equilibration took longer on desorption and the residual solid was very gassy. The desorption isotherm was superposable on but not coincident with a carbon dioxide-Sieve 5A isotherm.[3] Carbon dioxide was the only gaseous reaction product from this system. The sample was placed in an absorption train, and yielded only carbon dioxide gas, at temperatures below 150°, where pyrolysis of any residual $CHClF_2$ would not be anticipated.

Chlorodifluoromethane also was stored over outgassed Sieve 5A for three weeks at 25°, and analyzed chromatographically; it was found to contain 0.4% by volume of carbon dioxide which previously had not been present. The residual solid material showed predominantly carbon dioxide evolution when heated in a mass spectrometer to 1000°. No halogen acid or carbon monoxide was seen.

Similar experiments conducted with Linde Molecular Sieve 4A did not show the same change in the isotherms, but infrared spectra showed a strong carbonyl absorption at 4.20μ and unassigned new bands at 14μ in the final gas.

Both series of experiments resulted in a loss of surface area of the solid (*e.g.* from an initial value 566.6 sq.m./g. to a new value of 290.0 sq. m./g. for carbon dioxide on 4A at 25.0°) but no gross structural changes in the sieves caused by the action of $CHClF_2$ were seen by X-ray diffraction.

Halogen acid products subsequently were found in the solid residuum: they presumably are present in a fully ionized form, since they were not seen in the mass spectrometer.

The reaction appears similar to that observed by Park, *et al.*,[4] who obtained carbon dioxide on heating wet $CHClF_2$, the water in the present case being the constitutional water of the zeolite. However, the mechanism appears open since Barrer and Brook[5] suggested dehydrofluorination to explain the attack of $CHClF_2$ on natural zeolites, and Ayscough and Emeléus[6] remarked on the formation of carbon dioxide and SiF_4 when CF_3 radicals were studied in quartz. The evidence of Neilson and White[7] on the association of liquid $CHClF_2$, and the peculiar geometry of the Molecular Sieve lattice[1] make it impossible to rule out here an exchange mechanism based on the polarization of $CHClF_2$.

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[3] "Molecular Sieve Data Sheets," Linde Air Products Co., Tonawanda, N. Y.

[4] J. D. Park, *et al.*, *Ind. Eng. Chem.*, **39**, 354 (1947).

[5] R. M. Barrer and D. W. Brook, *Trans. Faraday Soc.*, **49**, 940 (1953).

[6] P. B. Ayscough and H. J. Emeléus, *J. Chem. Soc.*, 3381 (1954).

[7] E. F. Neilson and D. White, THIS JOURNAL, **79**, 5620 (1957).

THE SITES OF REDUCTION AND BASE-CATALYZED HYDROGEN-EXCHANGE IN N^1-METHYLNICOTINAMIDE IODIDE[1]

Sir:

Previous work on the dithionite-reduction of N^1-methylnicotinamide indicated that hydrogen is added to the 4-position.[2,3,4,5] Our nuclear magnetic resonance (n.m.r.) data substantiate this, and further show that base-catalyzed hydrogen-exchange occurs at the 2- and 6-positions. Such exchange was noticed only at the 2-position of diphosphopyridine nucleotide (DPN).[6]

The assignment of sites was accomplished by comparing the n.m.r. spectra of N^1-methylnicotinamide iodide (I), 2,6-dideuterio-N^1-methylnicotinamide iodide (II), N^1-methylnicotinamide chloride partially 4-deuteriated (III),[3] and N^1-benzylnicotinamide chloride (IV). II was formed by dissolving 0.025 g. of I in 0.5 cc. of D_2O, containing 0.075 g. of Na_2CO_3. The exchange was completed by heating to 100°.

The spectrum of the ring protons of I consists of a single peak with relative area 1 unit at -114 cycles (benzene = zero cycles. Field strength 40 Mc.), three peaks at -104, -100 and -95 cycles with total relative area 2 units, four peaks at -77, -71, -69 and -62 cycles with total relative area 1 unit. In the spectrum of II, the peaks at -114 and -100 cycles had disappeared, the peak at -104 cycles was reduced in size, and the peaks centered about -70 cycles had collapsed into a 1:1 doublet. In III, the peak at -95 cycles was greatly reduced in size, and the peaks centered about -70 cycles partially collapsed into a doublet. The spectrum of IV is similar to that of I.

Because of the electronegativity and the formal charge of N^1, the 2- and 6-protons are shifted down field.[7] The carboxamide group should similarly affect the 2- and 4-protons. Thus the peak at -114 cycles may be assigned to the 2-proton and the group centered about -70 cycles to the 5-proton. The 2-proton could give a single line since there are no hydrogens on the adjacent atoms. The 5-proton line should be split by the 4- and 6-protons into two overlapping doublets or approximately a 1:2:1 triplet. The remaining spectrum, centered about -100 cycles, must therefore be assigned to the 4- and 6-protons.

Since N^1-methylpyridinium iodide exchanges its 2- and 6-protons in aqueous Na_2CO_3 solution[8] and

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[1] This work was supported in part by a grant from Research Corporation.

[2] M. E. Pullman, A. San Pietro and S. P. Colowick, *J. Biol. Chem.*, **206**, 129 (1954).

[3] G. W. Rafter and S. P. Colowick, *ibid.*, **209**, 773 (1954).

[4] M. B. Yarmolinsky and S. P. Colowick, *Biochim. et Biophys. Acta*, **20**, 177 (1956).

[5] D. Mauzerall and F. H. Westheimer, THIS JOURNAL, **77**, 2261 (1955).

[6] A. San Pietro, *J. Biol. Chem.*, **217**, 589 (1955).

[7] This is consistent with the results of W. G. Schneider, H. J. Bernstein and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

[8] H. E. Dubb, M. Saunders and J. H. Wang, to be published.

since in obtaining II from I the 2-proton peak disappeared instantaneously, followed by the slower disappearance of the peak at −100 cycles and a simultaneous diminution of the peak at −104 cycles, we may assign the peaks at −104 and −100 cycles to the 6-proton and the peaks at −104 and −95 cycles to the 4-proton. The above observation also shows that the 2-proton exchanges much faster than the 6-proton.

In the spectrum of III, the 4-proton lines partially disappeared and the 5-proton lines collapsed into a doublet. Therefore, the reduction must have occured at the 4-position.[9]

[9] Westheimer and Hutton recently independently obtained consistent n.m.r. data (to be published).

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CRYSTALLINE POLYMERS OF METHYL METHACRYLATE

Sir:

Recently we have synthesized several crystallizable forms of poly-(methyl methacrylate) by means of stereospecific polymerizations effected by apparently homogeneous free radical and anionic initiating systems. Crystallization was effected by solvent treatment in borderline solvents such as 4-heptanone. Three polymer types (I, II, III) have been characterized by their different X-ray diffraction patterns as well as by differences in their properties, not only in the crystalline but also in the amorphous states (Table I).

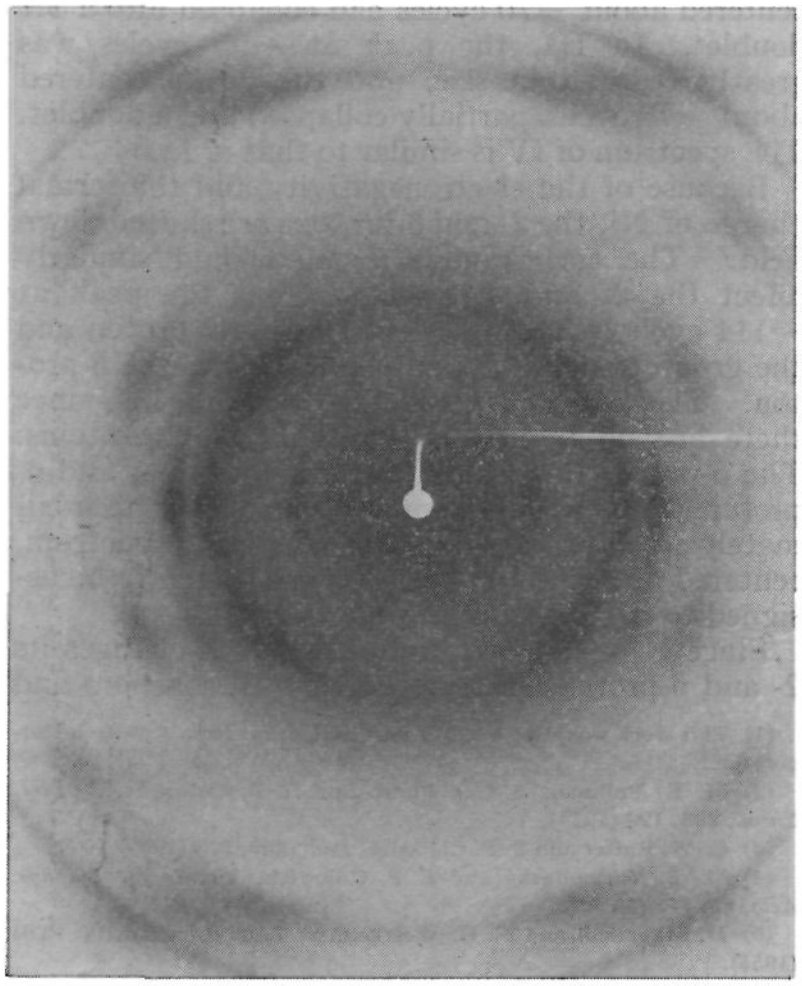

Fig. 1.—X-Ray fiber diffraction pattern of type II PMMA; stretch orientation vertical; exposure calibrated by 2.81 Å.; NaCl line; Ni filtered CuK radiation.

TABLE I

PROPERTIES OF POLYMERS OF METHYL METHACRYLATE

	From vol.-temp. meas.			
Type	Glass temp. T_g, °C.	Melting point, T_m, °C.	Density of amorphous polymer at 30°, g./ml.[3]	Presumed chain configuration
I	115	(>200)[a]	1.19	Isotactic
II	45	160	1.22	Syndiotactic
III	60–95	170	1.20–1.22	Isotactic - syndiotactic block copolymer
Conventional	104	. . .	1.188	Essentially random

[a] Extrapolated from data on concentrated solutions.

The ability of these polymers to crystallize is ascribed to unusually uniform chain structure resulting from isotactic or syndiotactic[1] arrangement of configurations at the pseudoasymmetric carbon atoms. In this respect they are similar to certain crystallizable linear polymers prepared by Natta[1] by means of heterogeneous solid catalysts. A preliminary assignment of the configuration of the various types of poly-(methyl methacrylate), based on evidence to be published later, is shown in Table I.

Type I poly-(methyl methacrylate) results from free radical polymerizations conducted at low temperature, as well as from anionic polymerizations in highly solvating media, such as those initiated by 9-fluorenyllithium in 1,2-dimethoxyethane at −60°. The stereospecificity of these polymerizations is believed to arise from small differences in the free energies of the two transition states, such as the differences which may result from interaction of the groups of the last and penultimate monomer units at each monomer addition step.

Type II poly-(methyl methacrylate) is prepared by anionic polymerizations initiated by organolithium compounds in hydrocarbons. Thus 9-fluorenyllithium at −60° in toluene produces quantitative yields of type II polymers. Under these conditions chain propagation involves an ion pair rather than free ions; the lithium counterion apparently is involved intimately in the transition state.[2] An X-ray diffraction pattern of a crystalline type II fiber is shown in Fig. 1.

Anionic polymerizations at low temperature in media of moderate solvating power for cations produce poly-(methyl methacrylate) of type III. Such polymers are produced by 9-fluorenyllithium at −70° in toluene containing small amounts of dioxane. These conditions are intermediate between those leading to types I and II. Intimate mixtures of types I and II crystallize to give the same diffraction patterns as those obtained from type III. However, while the mixtures may be separated by fractionations under special conditions, it has not been possible to obtain an equivalent separation of type III polymers prepared directly. This evidence suggests that the latter polymers consist of alternating sequences of isotactic and syndiotactic structures. This "block

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[1] *Cf.* G. Natta and P. Corradini, *Atti acad. nazl. Lincei* (Series 8), **18**, 19–27 (1955); G. Natta, F. Danusso, and G. Moraglio, *Makromol. Chem.*, **20**, 37–45 (1956); G. Natta, *Angew. Chem.*, **68**, 393–403 (1956).

[2] *Cf.* F. W. Stavely and co-workers, *Ind. Eng. Chem.*, **48**, 77 (1956); H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 245 (1957).