# N-Methylated Oligo(*p*-phenyleneterephthalamide)s with a High Propensity for Intramolecular Cyclization

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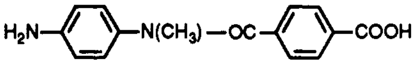
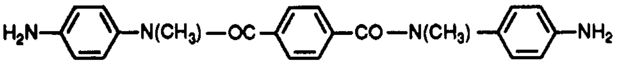
## Introduction

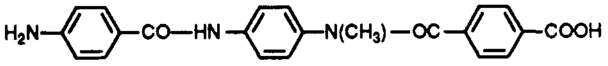
The demand for more easily processable substitutes for poly(*p*-phenyleneterephthalamide) (PPTA) has led some authors[1-4] to investigate the effects of N-alkylation on this aromatic polyamide. These studies have shown that N-alkylation, even if limited, markedly alters the properties of PPTA, causing, in particular, the loss of the ability to form liquid-crystalline solutions. This effect has been attributed to a plausible[5,6] strong preference of the N-substituted amide groups for the cis (*E*) configuration and to the consequent drastic reduction in polymer stiffness.[4,6,7] We present here additional indirect evidence for this preference. The evidence is based on results that we have obtained from polycondensation reactions carried out with *N*-(4-aminophenyl)-*N*-methylterephthalamic acid (MI), *N,N'*-bis(4-aminophenyl)-*N,N'*-dimethylterephthalamide (MII), or *N*-[4-[(4-aminobenzoyl)amino]phenyl]-*N*-methylterephthalamic acid (MIII) as monomer.



MI



MII



MIII

The results of this work, which we have undertaken with the aim to study the influence of constitutional regularity[8] on the properties of partially N-methylated PPTAs, show that oligo(*p*-phenyleneterephthalamide)s with N-methylated groups can have a high propensity for intramolecular cyclization.

## Experimental Section

The synthesis and purification of the monomers MI-MIII will be described elsewhere.[9] $^1$H NMR spectra of the purified monomers [MI $\delta$ 12.94 (1 H, br, COOH), 8.32 (2 H, s, NH$_2$), 7.75 (2 H, d, Ar H), 7.32 (2 H, d, Ar H), 6.83 (2 H, d, Ar H), 6.44 (2 H, d, Ar H), 3.28 (3 H, s, CH$_3$); MII $\delta$ 6.99 (4 H, s, Ar H), 6.66 (4 H, d, Ar H), 6.35 (4 H, d, Ar H), 5.11 (4 H, s, NH$_2$), 3.22 (6 H, s, CH$_3$); MIII $\delta$ 13.07 (1 H, br, COOH), 9.75 (2 H, s, NH$_2$), 7.77 (2 H, d, Ar H), 7.66 (2 H, d, Ar H), 7.62 (2 H, d, Ar H), 7.34 (2 H, d, Ar H), 7.11 (2 H, d, Ar H), 6.57 (2 H, d, Ar H), 5.76 (2 H, s, NH$_2$), 3.36 (3 H, s, CH$_3$); ~10 mg/mL in DMSO-$d_6$; 25 °C; reference TMS] gave no indication of impurities.

The polycondensation reactions were carried out as described in the following representative examples.

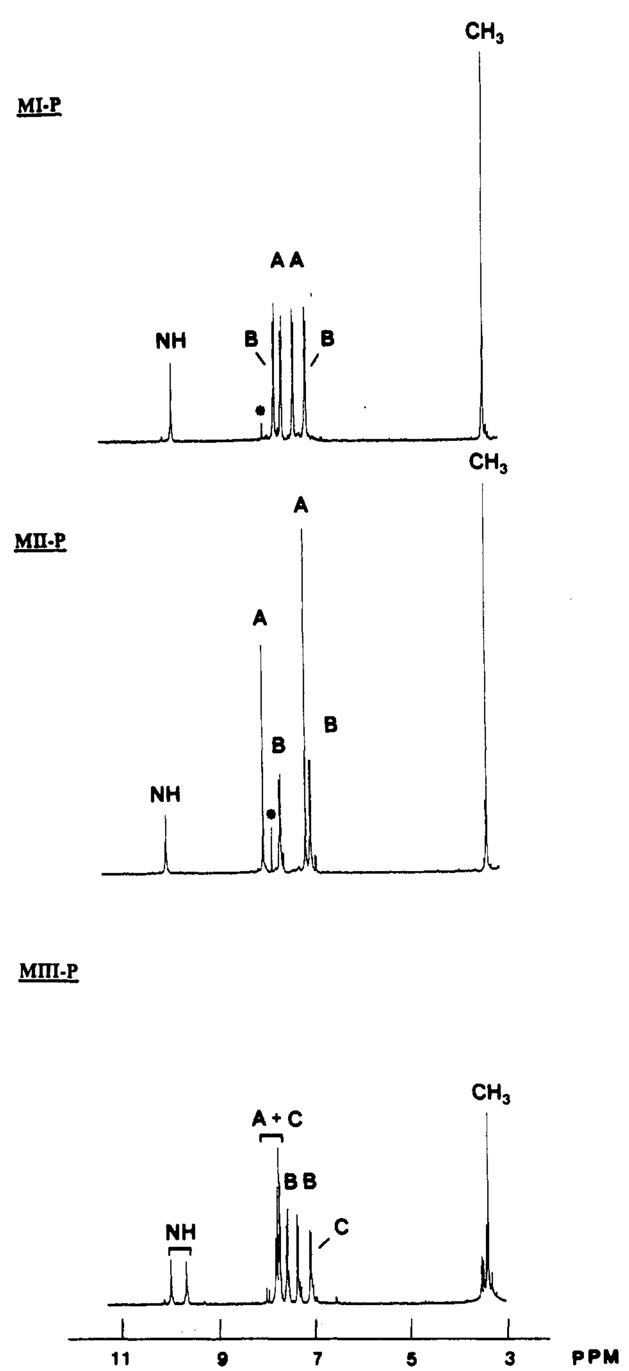


**Figure 1.** 300-MHz $^1$H NMR spectra of three representative products of polycondensation reactions carried out with MI, MII, or MIII as monomers or comonomers [DMSO-$d_6$ + LiCl (0.2%), 120 °C]. A, B, and C indicate the aromatic protons in the units A = OC-$C_6H_4$-CO, B = HN-$C_6H_4$-N(CH$_3$), and C = HN-$C_6H_4$-CO. The assignments are based on results obtained with the monomers and with model compounds.[9] The signal denoted by an asterisk is given by traces of dimethylformamide, a solvent which has been used for fractionating the products.

**Triphenyl Phosphite as Condensing Agent.**[10] MI (0.451 g, 1.47 mmol) and triphenyl phosphite (Fluka, 0.456 g, 1.47 mmol) were dissolved in a mixture of 1-methyl-2-pyrrolidinone (NMP) (Fluka puriss., 2.94 mL), pyridine (0.74 mL), and LiCl (0.15 g), and the solution was heated at 100 °C for 6 h with stirring under nitrogen. The solution was then poured into 15 mL of methanol, and the precipitated product was isolated by filtration, washed exhaustively with methanol and with water, and dried. Yield, 0.28 g.

**Phenylphosphonic Anhydride as Condensing Agent.**[11] MII (0.277 g, 0.735 mmol), terephthalic acid (0.122 g, 0.735 mmol), and phenylphosphonic anhydride (0.611 g, 1.47 mmol; prepared as described in the literature[12]) were dissolved in a mixture of NMP (0.74 mL) and pyridine (0.24 mL), and the solution was

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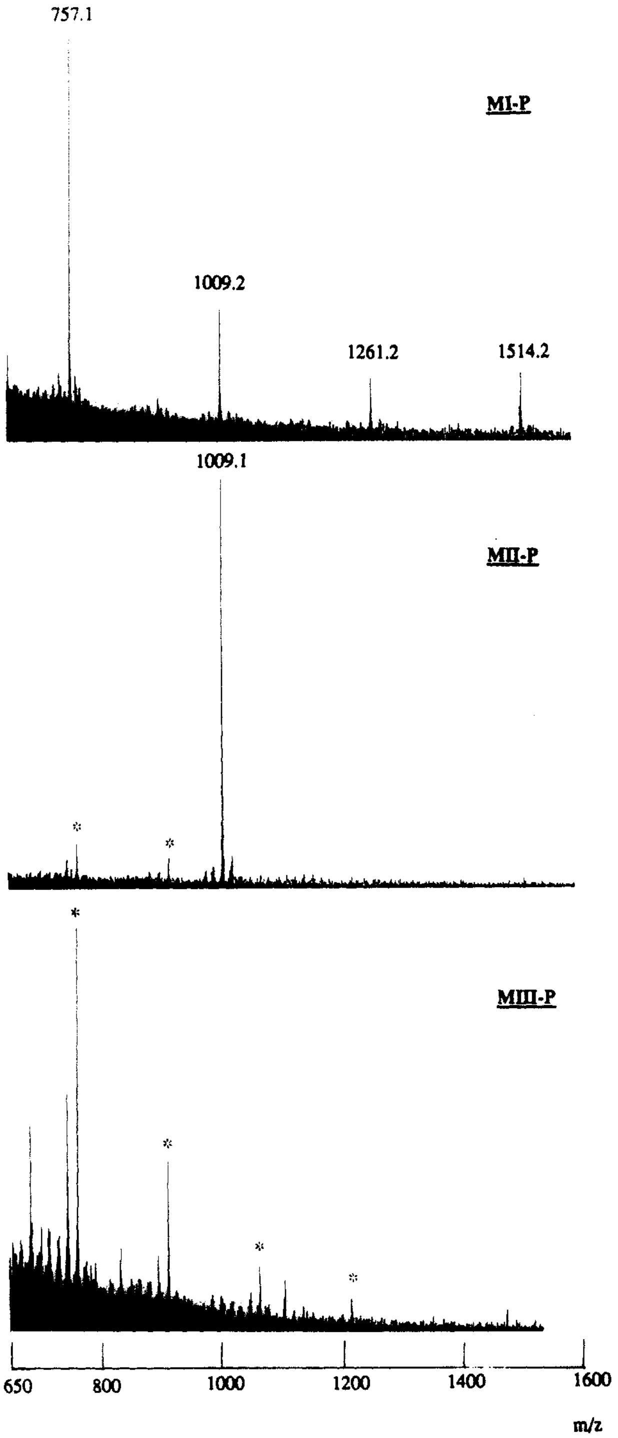

**Figure 2.** Partial, positive-ion FAB mass spectra of the polycondensation products, the NMR spectra of which are shown in Figure 1. The peaks marked with an asterisk are due to the matrix (3-nitrobenzyl alcohol).

heated at 80 °C for 3 h. The product was isolated using the same procedure as in the above example. Yield, 0.34 g.

**N-Silylation Method.**[13] Freshly sublimated terephthaloyl chloride (0.702 g, 3.46 mmol) was added to a cold solution (−78 °C) of di-*N*-trimethylsilyl-MII (1.80 g, 3.46 mmol; prepared following the literature[14]) in NMP (6.9 mL). The mixture was stirred at −10 °C for 3 h. The product was isolated in the usual way (see above). Yield, 0.86 g.

The FAB mass spectra were obtained on a Vacuum Generators (VG) ZAB2-SEQ instrument, by using a Cs gun as primary ion source. The matrix for the samples to be bombarded was a 3-nitrobenzyl alcohol/trifluoroacetic acid (1/1 v/v) mixture.

Inherent viscosities, $\eta_{inh} = \ln \eta/\eta_s C$, where $\eta$ is the solution viscosity, $\eta_s$ that of the solvent, and $C$ the mass concentration, were approximated by measuring flow times in an Ostwald viscometer at $C$ = 0.5 g/dL and 25 °C in $H_2SO_4$ (96%) and substituting measured times for viscosities.

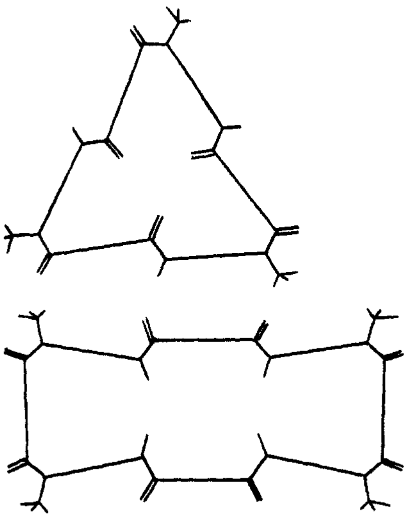

**Figure 3.** Sketches of the cyclic trimer of MI (top) and of the mixed cyclic dimer of MII and terephthalic acid (bottom) in conformations with coplanar amide bonds. The *p*-phenylene rings are omitted for clarity.

## Results and Discussion

Most of the polycondensation reactions were carried out according to the procedure of Yamazaki,[10] by using triphenyl phosphite as condensing agent. A few reactions, in which MI or MII and terephthalic acid were used as monomers, were performed following the method of Ueda and Honma[11] by using phenylphosphonic anhydride as condensing agent. Finally, some polycondensation reactions were carried out according to the procedure of Oishi et al.,[13] the monomers being in this cases the di-trimethylsilylated derivative of MII and terephthalic acid dichloride. The products (MI–Ps) obtained from MI and those (MII–Ps) obtained from MII and terephthalic acid or terephthalic acid dichloride exhibited very low values (between 0.1 and 0.2 dL/g) of the inherent viscosity, $\eta_{inh}$; the products (MIII-Ps) obtained from MIII were characterized by values between 0.4 and 0.5 dL/g. These $\eta_{inh}$ values did not change substantially by further fractionation of the products. Surprisingly, the $^1H$ NMR spectra of the products display the features (Figure 1) one would expect for polycondensation products obtained at relatively high extents of reaction [apparent absence or very low intensity of signals which might be contributed by protons at the ends of the polymer chains and approximate ratio of 1 to 3 (MI-Ps and MII-Ps) or 2 to 3 (MIII-Ps) for the intensities of the NH and $CH_3$ signals]. Thus, it would appear that the low inherent viscosities exhibited by these products, rather than being the consequence of very low molecular weights, simply reflect a viscosimetric behavior which appears to be typical[4] for N-alkylated PPTAs. For MI-Ps and MII-Ps, however, the low inherent viscosities derive, in large part at least, from another reason.

As shown in Figure 2, the partial mass spectra of MI-Ps present a series of pronounced peaks at *m/z* values of 757.1, 1009.2, 1261.2, and 1514.2, and those of MII-Ps present a conspicuous peak at *m/z* 1009.1. These are the *m/z* values expected for the protonated molecular ions [$(M + H)^+$ ions] of the cyclic tri-, tetra-, penta-, and hexamer of MI and of the mixed cyclic dimer of MII and terephthalic acid, respectively. On the basis of the NMR features, these cyclic oligomers appear to be present in fairly large amounts both in MI-Ps and in MII-Ps. It is, therefore, the presence of these cyclic oligomers that is mainly responsible for the low inherent viscosities of these products.

That these oligomers can so readily form implies that their linear precursors tend to bend at each N-methylated amide group. In this case, the probability for ring closure must be relatively high. Molecular models show that rings of the cyclic trimer of MI and of the mixed cyclic dimer of MII and terephthalic acid, such as those schematically shown in Figure 3, can be built with standard bond lengths and coplanar amide groups with virtually no or very little strain in the bond angles.

Interestingly, cyclic oligomers do not appear to occur in MIII-Ps. Apparently, the $N(CH)_3$ groups of the linear oligomers of MIII are already too far apart for an encounter of the chain ends to be very likely.

The synthesis by polycondensation of a few N-methylated, aromatic polyamides, such as wholly N-methylated PPTA[15] and some N-methylated poly(p-benzamide)s,[16] has been reported, but the possibility of concomitant cyclization reactions does not seem to have been considered. In light of the results presented here, these polyamides may have been contaminated by sizable amounts of cyclic oligomers.

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