3112 *Macromolecules* **1997,** *30,* 3112−3117

Communications to the Editor

Synthesis and Polycondensation of Novel Nitroaromatic Monomers. 2. Wholly Ordered Polymers of *N,N′*-Bis(4-amino-3-nitrophenyl)terephthalamide and *N,N′*-Bis[4-((4-amino-3-nitrophenyl)carbamoyl)phenyl]terephthalamide

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Received June 14, 1996
Revised Manuscript Received August 26, 1996

Introduction. Polycondensation of unsymmetrical monomers generally leads to polymers of irregular structure, sometimes referred to as "internal copolymers". However, the degree of order of polymers from unsymmetrical monomers can vary from highly irregular structures to wholly ordered ones depending upon the reactivity of the functional groups employed and/or the conditions under which the polycondensation occurs. Examples of the formation of partially ordered to wholly ordered poly(ester-amide)s,[2] poly(hydrazide-amide)s,[3−6] and poly(imide-hydrazide)s[7,8] have been reported.

Recently Suter and co-workers[9] showed that an unsymmetrical monomer, 2-nitro-1,4-phenylenediamine (NPPD) can be polycondensed (eq 1) (Scheme 1) with terephthaloyl chloride (TCl) to give a polymer, NPPD-T, having various degrees of order depending on the rate of addition of TCl. It is reasonable to presume that obtaining wholly (or very nearly so) ordered NPPD-T by slow addition of TCl involves the initial formation (eq 2) of a symmetrical bis(amide) intermediate, *N,N′*-bis(4-amino-3-nitrophenyl)terephthalamide, T(NPPD)$_2$, which undergoes further polycondensation *in situ*.

In the present communication we report the direct synthesis of T(NPPD)$_2$ and its polycondensation (eq 3) to give wholly ordered, *i.e.* regular, NPPD-T by an unequivocal route. Earlier we reported the novel synthesis of 4,4′-diamino-3′-nitrobezanilide (DNB) and its low-temperature polycondensation (eq 4) with TCl.[10] We now report the direct synthesis of *N,N′*-bis[4-((4-amino-3-nitrophenyl)carbamoyl)phenyl]terephthalamide, T(DNB)$_2$, which is postulated to be an intermediate in the low-temperature polycondensation (eq 5) of TCl with DNB. Unlike our earlier reported synthesis of DNB-T, the present synthesis (eq 6) can yield only the wholly ordered, *i.e.* regular, DNB-T because it is synthesized from the symmetrical monomer, T(DNB)$_2$.

Experimental Section. Materials. *p*-Aminobenzoic acid (PABA), terephthalic acid (TA), and lithium chloride, Aldrich, were dried over P$_2$O$_5$ under reduced pressure. Pyridine (Py), Aldrich, was refluxed and distilled first over potassium hydroxide and then over calcium hydride. *N*-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), and hexane, Fluka products, were freshly distilled over calcium hydride. Triphenyl phosphite (TPP), Aldrich, was freshly distilled under reduced pressure. All of the above liquids were deaerated with argon and stored over molecular sieves under an argon atmosphere. 2-Nitro-1,4-phenylenediamine (NPPD), Aldrich, was sublimed under reduced pressure prior to use. Terephthaloyl chloride (TCl), Aldrich, was distilled under reduced pressure and crystallized from anhydrous hexane. Sulfuric acid (96%), Fluka, was used as received.

NMP containing 5% dissolved lithium chloride was prepared by stirring with a magnetic bar just prior to use in a flame-dried flask (connected to an argon line regulated by a mercury bubbler *via* a three-way stopcock with a rubber septum on the up side) and deaerated with argon using three freeze−pump−thaw cycles.

Preparation of Monomers. 4,4′-Diamino-3-nitrobenzanilide, DNB. DNB was prepared as reported earlier[10] *via* condensation of PABA with NPPD under Yamazaki reaction conditions.[11]

***N,N′*-Bis(4-amino-3-nitrophenyl)terephthalamide, T(NPPD)$_2$.** A two-neck round-bottom 250 mL flask (equipped with a magnetic bar, a reflux condenser connected with an argon line, and a three-way stopcock with a rubber septum, likewise connected with the gas line) was deaerated and flame dried using three freeze−pump−thaw cycles. While under argon flow, the flask was charged with 6.126 g (40 mmol) of NPPD and 3.323 g (20 mmol) of TA. NMP (36 mL) and Py (30 mL) were then added by syringe and the flask was deaerated again. The reaction mixture was heated under stirring at 100 °C for 10 min and left to cool for 10 min, and then 11.6 mL (44 mmol) of TPP was added by syringe. After stirring at 100−110 °C for 3 h, the resulting solution was cooled and poured into methanol. The precipitate was filtered on a Buchner funnel and then purified by stirring in methanol at room temperature for 2 h, filtered again and washed with methanol on the filter. The T(NPPD)$_2$ obtained was finally dried over P$_2$O$_5$: yield 7.7 g (89%); DSC 373 °C (small exothermic peak), 389 °C (large exothermic peak). Anal. Theory (for $C_{20}H_{16}N_6O_6$): C, 55.05; H, 3.70; N, 19.26. Found: C, 55.10; H, 3.69; N, 19.00. ^{1}H NMR (DMSO-d_6): δ 7.05 (2H, d, *J* 9.2 Hz), 7.44 (4H, s), 7.80 (2H, dd, *J* 2.4 and 9.2 Hz), 8.09 (4H, s), 8.56 (2H, d, *J* 2.4 Hz), 10.41 (2H, s).

***N,N′*-Bis[4-((4-amino-3-nitrophenyl)carbamoyl)phenyl]terephthalamide, T(DNB)$_2$.** This monomer was prepared as above using either terephthalic acid with DNB or using *N,N′*-bis(4-carboxyphenyl)terephthalamide, T(PABA)$_2$, with NPPD. The synthesis of T(PABA)$_2$ is given below.

***N,N′*-Bis(4-carboxyphenyl)terephthalamide T(PABA)$_2$.** A two-neck round-bottom 250 mL flask (equipped with a magnetic bar, a gas inlet connected

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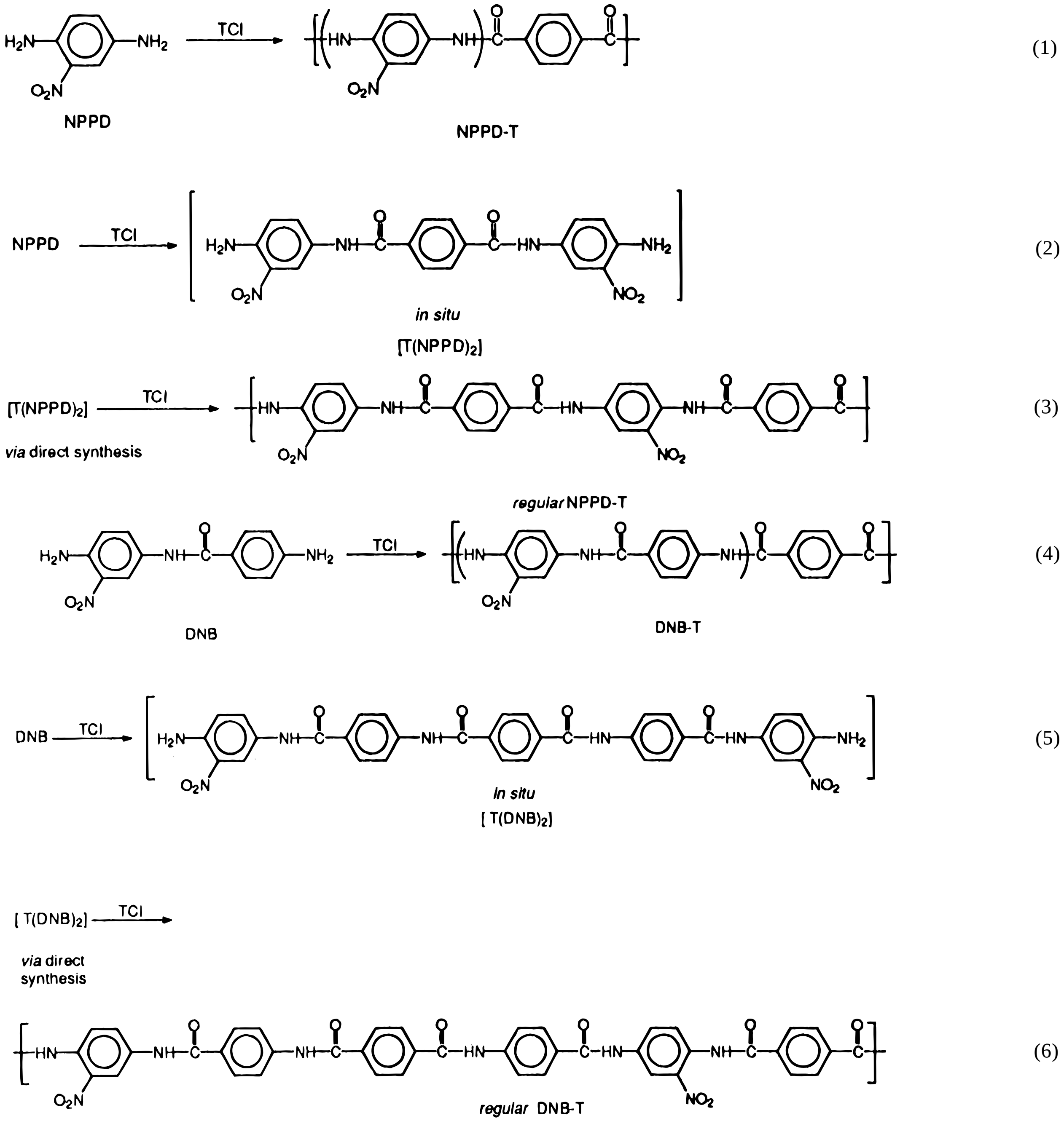
S0024-9297(96)00861-3 CCC: $14.00

Scheme 1



with the argon line, and a rubber septum) was deaerated and flame dried using three freeze–pump–thaw cycles. While under argon flow, the flask was charged with 8.228 g (60 mmol) of PABA and 80 mL of NMP was added by syringe; then the flask was deaerated again. The reaction mixture was stirred at room temperature for 30 min and cooled to 0 °C, and 4.060 g (20 mmol) of TCl was added all at once. After stirring for 15 min at 0 °C and 30 min at room temperature, the reaction solution was poured into a mixture of ice and water. The precipitate was filtered on a Buchner funnel and then purified by stirring in hot methanol for 2 h. Upon cooling, the white crystalline product was filtered off again and washed with methanol on the filter. The T(PABA)$_2$ was finally dried over P_2O_5: yield 7.6 g (94%); DSC 437 °C (endothermic peak). Anal. Theory (for $C_{22}H_{16}N_2O_6$): C, 65.35; H, 3.99; N, 6.93. Found: C, 65.20; H, 4.10; N, 7.12. ^{1}H NMR (DMSO-d_6): δ 7.97 (8H, s), 8.13 (4H, s),10.71 (2H, s), 12.80 (2H, s).

T(DNB)$_2$ from T(PABA)$_2$ and NPPD. A two-neck round-bottom 50 mL flask [equipped with a magnetic bar, a reflux condenser connected with an argon line, and a three-way stopcock with a rubber septum, likewise connected with the gas line] was deaerated and flame dried using three freeze–pump–thaw cycles. While under argon flow, the flask was charged with 2.020 g (5 mmol) of T(PABA)$_2$ and 1.684 g (11 mmol) of NPPD. NMP (9 mL) and Py (7.5 mL) were then added by syringe, and the flask was deaerated again. The reaction mixture was heated under stirring at 100 °C for 10 min, and 2.88 mL (11 mmol) TPP was added by syringe. After stirring at 100–110 °C for 6 h, the resulting solution was cooled to 0 °C and an orange precipitate filtered onto a Buchner funnel. The product was washed several times with water on the filter, stirred in a beaker with water, and then filtered again. The obtained T(DNB)$_2$ was finally dried over P_2O_5: yield 2.41 g (72%); DSC 397 °C (exothermic peak). Anal.

Table 1. Low-Temperature Polycondensation of NPPD and T(NPPD)$_2$ with TCl[a,b]

sample no.	polymer	diamine	final conc, wt %[c]	η_{inh}[d]	$[\eta]$[d]
1	NPPD-T (non regular)	NPPD	30.0	2.19	2.20
2	NPPD-T (non regular)	NPPD	5.0	2.62	2.59
3	NPPD-T (regular)	T(NPPD)$_2$	5.0	2.00 (5.35)[e]	2.04

[a] All polymerizations were carried out in NMP containing 5% dissolved LiCl; the reactants were 10 mmol each for the nonregular polymers and 5 mmol each for the regular ones. [b] Initial concentration (wt %) = 30; concentration based on polymer yield. [c] Concentration based on polymer yield. [d] Inherent (c = 0.1 g/dL) and intrinsic viscosities (dL/g) were determined in concentrated sulfuric acid at 25 °C. [e] Value in parentheses is inherent viscosity determined in DMAc containing 3% LiCl. This sample also had an inherent viscosity value of 4.75 determined in dimethylformamide containing 5% dissolved LiCl.

Theory (for $C_{34}H_{26}N_8O_8$): C, 60.53; H, 3.88; N, 16.61. Found: C, 60.20; H, 4.10; N, 15.88. ^{1}H NMR (DMSO-d_6): δ 7.04 (2H, d, J 9.1 Hz), 7.40 (4H, s), 7.80 (2H, dd, J 2.5 and 9.1 Hz), 7.99 (8H, s), 8.15 (4H, s), 8.55 (2H, d, J 2.5 Hz), 10.19 (2H, s), 10.69 (2H, s).

T(DNB)$_2$ from TA and DNB. The synthesis was performed using the procedure reported immediately above. Thus, 0.544 g (2 mmol) of DNB and 0.183 g (1.1 mmol) of TA were reacted in a mixture of 1.5 mL of Py and 1.8 mL of NMP containing 0.14 g of LiCl. After addition of 0.58 mL (2.2 mmol) of TPP, the reaction mixture was stirred at 100−110 °C for 2 h and worked up as above to give 0.66 g (98%) of pure T(DNB)$_2$.

Polymerizations. Nonregular NPPD-T from NPPD and TCl: Concentrated-Solution Method. A three-neck round-bottom 250 mL flask [equipped with a mechanical stirrer, an argon inlet and a rubber septum] was deaerated and flame dried using three freeze−pump−thaw cycles. While under argon flow, the flask was charged with 1.531 g (10 mmol) of NPPD, 9.5 mL of NMP containing 5% LiCl was added by syringe, and the flask was deaerated again. The reaction mixture was heated under stirring at 60 °C for 15 min in order to dissolve the diamine completely. The solution was then cooled to 0 °C, and 2.030 g (10 mmol) of TCl was added all at once with vigorous stirring. After 10 min, the solution became highly viscous and stuck to the wall of the flask. After stirring at 0 °C for 2 h and overnight at room temperature, the reaction mixture (a sticky gel) was diluted with 50 mL of NMP/5% LiCl and stirred for 1 h. The mixture was then poured into water contained in a blender jar, finely chopped, and filtered. The crude product was purified by stirring in hot water for 2 h and in hot methanol for 2 h and finally by extraction overnight with methanol in a Soxhlet. After drying at 100 °C under 5 mmHg pressure for 6 h, 2.82 g (99.6%) of dark orange polymer was obtained (sample 1, Table 1).

Nonregular NPPD-T from T(NPPD)$_2$ and TCl: Diluted-Solution Method. Using an apparatus and a procedure similar to that reported above, 1.531 g (10 mmol) of NPPD in 9.5 mL of NMP containing 5% LiCl was reacted with 2.030 g (10 mmol) of TCl at 0 °C. When the solution became highly viscous and stuck to the wall of the flask (*ca.* 10 min), 5 mL of precooled (0 °C) NMP/5% LiCl was added by syringe. After *ca.* 20 min the reaction mixture again became highly viscous and an additional 5 mL of NMP/5% LiCl was added. The same operation was repeated over the course of 5 h with a total addition of 47 mL of the NMP/5% LiCl solvent. Thus, a final polymer concentration of 5.0% by weight was reached from the initial one of 30% by weight. The viscous reaction mixture was stirred overnight at room temperature and then poured into water in a blender jar, finely chopped, and filtered. The crude product was purified as reported above to give 2.82 g (99.6%) of dark orange polymer (sample 2, Table 1).

Table 2. Low-Temperature Polycondensation of DNB and T(DNB)$_2$ with TCl[a,b]

sample no.	polymer	diamine	η_{inh}[c]	$[\eta]$[c]
1	DNB-T (non regular)	DNB	3.55 (7.00)[d,e]	3.45
2	DNB-T (regular)	T(DNB)$_2$	1.40 (3.12)[d]	1.32

[a] The polymerizations were carried out in NMP containing 5% dissolved LiCl; the reactants were 4 mmol each for the nonregular polymers and 3 mmol each for the regular one. [b] Initial concentration = 30 wt % and final concentration = 5 wt %; concentration based on polymer yield. [c] Inherent (c = 0.1 g/dL) and intrinsic viscosities (dL/g) were determined in concentrated sulfuric acid at 25 °C. [d] Value in parentheses is inherent viscosity determined in DMAc containing 3% LiCl. [e] This sample also had an inherent viscosity value of 4.75 determined in dimethylformamide containing 5% dissolved LiCl.

Regular NPPD-T from T(NPPD)$_2$ and TCl: Diluted-Solution Method. Using an apparatus and a procedure similar to that reported above, 2.180 g (5 mmol) of T(NPPD)$_2$ in 5 mL of NMP containing 5% LiCl was reacted with 1.015 g (5 mmol) of TCl at 0 °C. The crude product was purified as usual to give 99% of a dark orange polymer (sample 3, Table 1).

Nonregular DNB-T from DNB and TCl: Diluted-Solution Method. Using an apparatus and a procedure similar to that reported above, 1.088 g (4 mmol) of DNB was reacted with 0.812 g (4 mmol) of TCl in NMP containing 5% LiCl. The crude product was purified as usual to give a 96% yield of a dark orange polymer (Sample 1, Table 2).

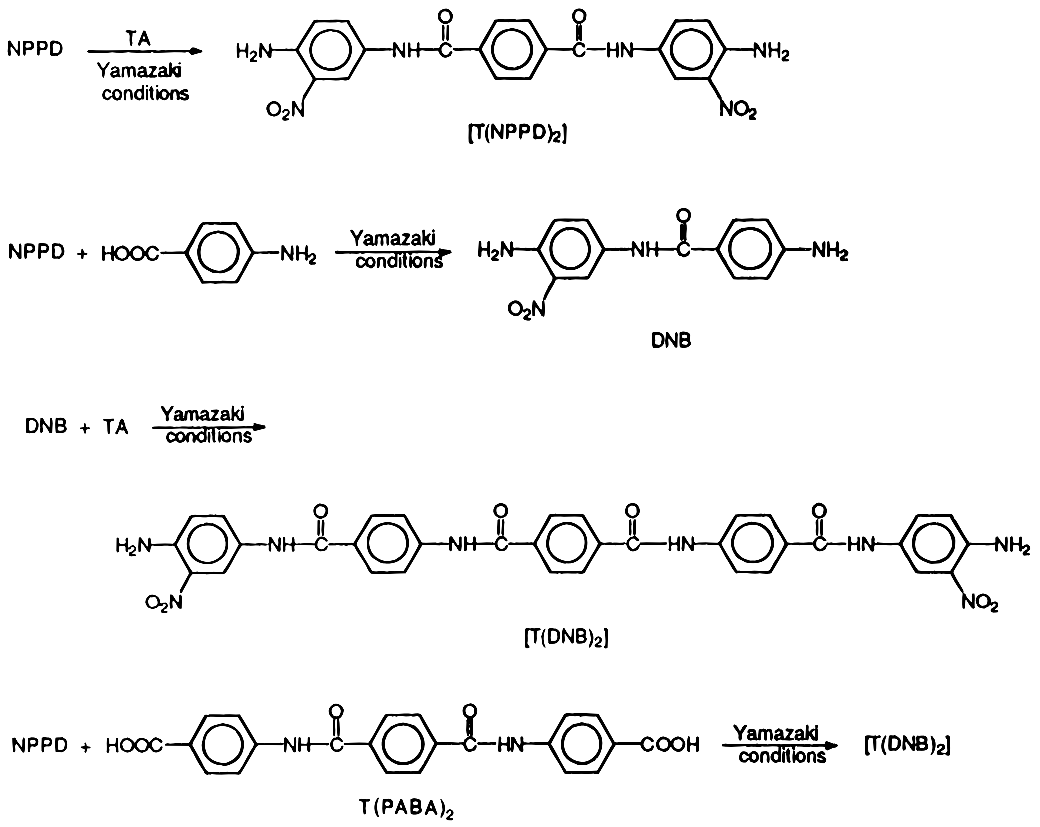
Regular DNB-T from T(DNB)$_2$ and TCl: Diluted-Solution Method. Using an apparatus and a procedure similar to that reported above, 2.022 g (3 mmol) of T(DNB)$_2$ was reacted with 0.609 g (3 mmol) of TCl in NMP containing 5% LiCl. The crude product was purified as usual to give a 95% yield of a dark orange polymer (sample 2, Table 2).

Characterization. ^{1}H NMR spectra were recorded at 200 MHz using a Varian Gemini 200 spectrometer with tetramethylsilane as the internal standard in DMSO-d_6 as solvent. Inherent and intrinsic viscosities were determined in 96% H_2SO_4 as previously described.[10] Thermal analysis (TGA and DSC) was also performed with the apparatus and technique described in a previous publication[12] (TGA: sample weight 4.1−5.3 mg, rate 10 °C/min. DSC: sample weight 1.12−1.35 mg, rate 20 °C/min) in the temperature range from room temperature to *ca.* 430 °C.

Results and Discussion. Synthesis of Monomers. Recently, we reported[10] that an amino group *ortho* to a nitro group is unreactive toward a carboxylic acid group under Yamazaki[11] or Higashi[13,14] conditions. This discovery permits the synthesis of some model compounds and monomers that otherwise might be rather difficult to prepare. Thus, it was possible to make and isolate in pure form *N*,*N*′-bis(4-amino-3-nitrophenyl)terephthalamide, T(NPPD)$_2$, by the reaction (eq 7) (Scheme 2) of NPPD and terephthalic acid (TA) under Yamazaki conditions.

Another monomer that can be produced in good yield and high purity is 4,4′-diamino-3′-nitrobenzanilide, DNB

Scheme 2



(7)

(8)

(9)

(10)

(eq 8). Reaction (eq 9) of DNB with TA under Yamazaki conditions produces *N*,*N*′-bis[4-((4-amino-3-nitrophenyl)carbamoyl)phenyl]terephthalamide, T(DNB)$_2$. This monomer can, alternatively, be produced by the reaction (eq 10) of NPPD and *N*,*N*′-bis(4-carboxyphenyl)terephthalamide, T(PABA)$_2$. (Note: T(PABA)$_2$ can be produced by the solution method reported here or by the interfacial method reported earlier.[15])

Polymerizations. Nonregular NPPD-T. NPPD was polymerized with TCl (eq 1) at the start in a very concentrated solution (*ca.* 30%). After the polycondensation was complete, the highly viscous solution, whichinitially stuck to the walls of the flask, was diluted to *ca.* 5%. The $[\eta] = 2.20$, of polymer prepared in this fashion, and referred to in the Experimental Section as having been prepared by the concentrated solution method, was lower than that of a similarly prepared polymer, $[\eta] = 2.59$, which was prepared by rapid dilution during polymerization (referred to as the diluted-solution method in the Experimental Section). The lower molecular weight of the first sample, as reflected by the lower $[\eta]$ value, may be attributed to the difficulty of TCl diffusing through a more viscous solution and consequently having a greater probability of reacting with solvent. For either polymer, the η_{inh} values obtained by us were only marginally higher to slightly inferior to those of nonregular NPPD-Ts reported by Suter and co-workers,[9] who used *N*-ethylpyrrolidinone as solvent to lower the probability of TCl reacting with the polymerization solvent.

Regular NPPD-T. The monomer T(NPPD)$_2$ was polymerized (eq 3) with TCl to give the same composition polymer as that of NPPD-T. But in this case the structure can only be that of regular NPPD-T. In other words, the rate of addition of TCl, which was critical for order in the case of NPPD-T prepared by the method of Suter and co-workers,[9] has no effect on the degree of order because order has been predetermined by use of the symmetrical monomer, T(NPPD)$_2$. Although regular NPPD-T apparently is of lower molecular weight than nonregular NPPD-T, as evidenced by a lower $[\eta]$ value (2.04 *vs* 2.59), the difference in molecular weight can probably be ascribed to the fact that the monomer, T(NPPD)$_2$, is probably more difficult to prepare in a highly purified form than is NPPD because the former was used as precipitated whereas the latter can be purified readily by recrystallization followed by sublimation (or merely by sublimation alone). It is of interest to note that samples of regular NPPD-T prepared by the kinetic control method of Suter and co-workers[9] had lower η_{inh} values than nonregular NPPD-T prepared by those authors (1.72 and 2.49 *vs* 2.55, 2.97, and 3.55).

Nonregular DNB-T. Earlier we reported[10] the synthesis of moderately high molecular weight ($\eta_{\mathrm{inh}} = 1.4$) DNB-T (eq 4), which probably has some degree of order and probably is amenable to a high degree of order if polymerized under certain reaction conditions, such as those reported by Suter and co-workers[9] for NPPD-T. But, as polymerized here (see Experimental Section), the polymer must be considered to be nonregular. The molecular weight of the polymer apparently is higher than our previously reported sample, as suggested by an appreciably higher inherent viscosity value ($\eta_{\mathrm{inh}} = 3.55$; $[\eta] = 3.45$).

Regular DNB-T. Regular, *i.e.*, wholly ordered, DNB-T was obtained by the polycondensation (eq 6) of T(DNB)$_2$ and TCl. The viscosity of the sample of regular DNB-T was considerably lower than that of the sample of nonregular DNB-T, possibly again, because of the difficulty of purification of the large monomer employed.

Thermal Behavior. TGA and DSC data for NPPD-T and DNB-T samples are collected in Figures 1 and 2, respectively. A weight loss observed at *ca.* 420 °C is in line with the results reported by Kim and Pearce[16] and,

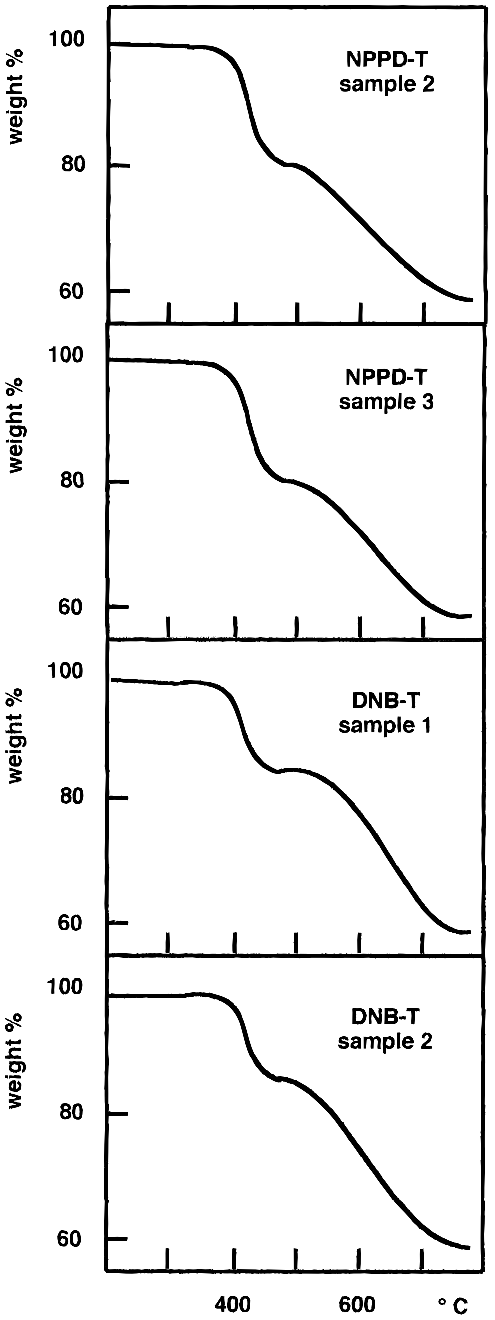


Figure 1. TGA profiles for the polymers included in Tables 1 and 2.

as they suggested, could result from thermally induced intramolecular eliminations of nitrous acid between the ring nitro and one hydrogen of the adjacent amide group, with formation of benzoxazole moieties in the polymer backbone. The DSC data (Figure 2) for all samples show only one peak at *ca.* 420 °C, which is well correlated with the chemical transformation revealed by TGA.

Conclusions. Although polymers of highly regular (or very nearly so) constitution can be prepared from unsymmetrical diamine monomers having an *ortho* nitro group adjacent to an amine group, polymers which are completely regular can be produced by the preparation of symmetrical diamine monomers containing nitro groups *ortho* to the amino groups. Using this method, special polymerization conditions relying on kinetic methods for constitutional order are not required. The symmetrical monomers that are required can be obtained readily by a synthesis which leads to coupling of an aromatic dicarboxylic acid with amino groups nonadjacent to *ortho* nitro groups. Thus, the diamine synthesis reported here is applicable to the preparation of monomers and model compounds.

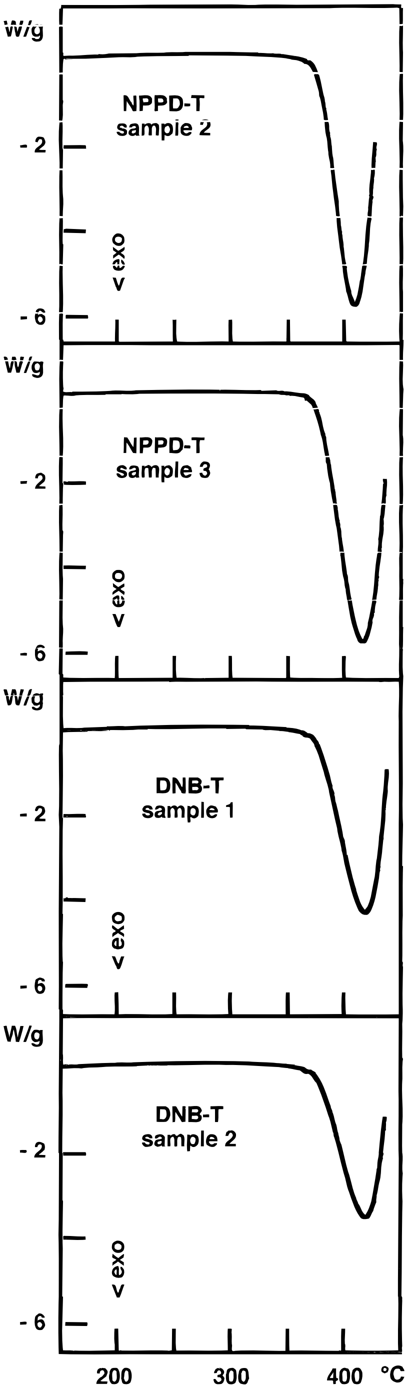


Figure 2. DSC profiles for the polymers included in Tables 1 and 2.

The lack of observation of liquid crystalline transitions below 430 °C for the samples examined confirms the rigid nature of the chain and indicates that the liquid crystalline phase cannot be induced thermotropically and could only be observed in lyotropic systems.

As previously suggested, the differential reactivity of amino groups with or without *ortho* nitro groups could be used for the preparation of well-tailored block copolymers. Work is underway for the preparation of triblock copolymers with exact sequences of ABA and BAB, where A is a rigid and B a flexible block.

Acknowledgment. This investigation was supported by Grant CI1*-CT93-0322 "Liquid Crystalline Copolymers Having Rigid and Flexible Blocks" of the Commission of the European Community, International Scientific Cooperation. N.N.C. acknowledges with thanks a grant from the European Community and additional support from the JEPA-LIMMAT Foundation. A.E.L. and J.P. acknowledge thanks for a travel grant from NATO, CRG 931191, and J.P. acknowledges with thanks support from the NSF, Grant CTS-9402055.

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MA960861L