Polymer Bulletin 11, 229–236 (1984)

Polymer Bulletin

Synthesis

Synthesis and Thermal Stability Evaluation of End-Capped Nylon 4 Oligomers

R. Bacskai

Chevron Research Company, Richmond, California 94802-0627, USA

SUMMARY

End-capped dimers, trimers, and tetramers of nylon 4 were prepared by stepwise synthesis using the p-nitrophenyl active ester coupling method. By thermal gravimetric analysis and gas chromatography, it was found that all of the oligomers studied are thermally unstable and decompose upon heating into pyrrolidone. The rate of oligomer decomposition was found to vary with the nature of the end group; maximum thermal stability was observed for a tetramer having acetoxy and n-propylamido end groups. The results indicate that linear sequences of γ-aminobutyryl units are inherently thermally unstable and have a strong tendency to revert into the thermodynamically more stable pyrrolidone ring.

INTRODUCTION

The preparation, physicochemical characterization, and fiber spinning of high molecular weight nylon 4 has been the subject of many investigations in recent years.[1,2] The great interest in this polymer arises from the fact that textile fibers of nylon 4 combine the good strength properties of conventional nylon 6 or 66 with the hydrophilicity of cotton.[3,4] The melt spinning of nylon 4 fibers is a challenging technical problem because the polymer decomposes into monomer near its melting point. Recent modifications in the chemistry of the polymerization, employing CO_2[5] or quaternary ammonium catalysts,[6] produced a polymer of improved thermal stability; but the so-called "new" nylon 4 is still considerably less stable than nylon 6 or 66.

The thermal instability of nylon 4 is believed to be caused by the fact that in the melt the polymer ⇄ monomer equilibrium lies completely on the side of the monomer.[3,6] End groups,[6] catalyst impurities,[6] and molecular weight distribution[5] also effect polymer stability; and it is not inconceivable that thermal decomposition is influenced by the presence of irregular structures[7] which act as "weak links."[4]

It is very difficult to assess the importance of these various effects in a high molecular weight polymer, such as nylon 4, because of the formidable purification and analytical problems. Therefore, it was of interest to synthesize low molecular weight nylon 4 oligomers with well-defined end groups, where purification and analysis can be accomplished by the techniques of classical organic chemistry. An examination of the thermal stability of oligomers should then provide useful information about the causes of thermal dissociation of nylon 4.

EXPERIMENTAL

Oligomer Synthesis

Benzyl p-nitrophenyl carbonate was prepared from benzyl chloroformate and p-nitrophenol by the method of Wolman and coworkers.[8] Melting point = 80°C; reported 79-80°C.

P-nitrophenyl carbobenzoxy-γ-aminobutyrate (I) was prepared from benzyl p-nitrophenyl carbonate and γ-aminobutyric acid in 78.8% yield by the method of Wolman.[8] Two crystallizations from 100% ethanol gave pure I; anal. calcd. for $C_{18}H_{18}O_6N_2$: C, 60.33%; H, 5.06%; N, 7.81%; found: C, 59.92%; H, 5.06%; N, 7.82%.

Methyl-γ-aminobutyrate hydrochloride was prepared by the method of Brenner and Huber.[9] Melting point, 122-124°C, reported 121.5-122.5°C.[10]

Methyl carbobenzoxy-γ-aminobutyryl-γ-aminobutyrate (II) and all of the other oligomers were prepared by Bodanszky's[11] method. A solution of 10.1 g of I and 5.15 g of methyl-γ-aminobutyrate hydrochloride in 26.4 g of dimethyl formamide was reacted with 3.6 g of triethylamine. The resulting precipitate was diluted with water and extracted with ethyl acetate. The organic layer was washed with water, N NH_4OH, water, N HCl, and water. Evaporation yielded 7.21 g solid. Recrystallization from 100% ethanol gave 4.5 g (47.4%) of pure II; anal. calcd. for $C_{17}H_{24}O_5N_2$: C, 60.70%; H, 7.19%; N, 8.33%; found: C, 60.65%; H, 7.28%; N, 8.18%.

Methyl carbobenzoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyrate (III). A solution of 1.35 g II and 60 ml of 15% HBr in acetic acid was allowed to stand at room temperature. The addition of ether produced a precipitate; it was washed with ether and dried at room temperature to give 1.14 g of white solid. The solid was dissolved in 4.8 ml dimethyl formamide, and the solution was mixed with 1.43 g of

I and 1.9 g of triethylamine. After standing overnight, 50 ml water was added to the reaction mixture. The white precipitate was washed with ethyl acetate, filtered, and dried. Yield = 0.80 g. Recrystallization from 100% ethanol gave 0.76 g (45.1%) pure III; anal. calcd. for $C_{21}H_{31}O_6N_3$: C, 59.84%; H, 7.41%; N, 9.97%; found: C, 59.68%; H, 7.34%; N, 9.97%.

Methyl carbobenzoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyrate (IV) was prepared from III and I. Yield of recrystallized IV = 79.7%; anal. calcd. for $C_{25}H_{38}O_7N_4$: C, 59.27%; H, 7.56%; N, 11.06%; found: C, 59.13%; H, 7.57%; N, 11.27%.

Methyl acetoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyrate (IIIa) and methyl acetoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyrate (IVa) were prepared from III and IV, respectively. Replacement of the carbobenzoxy group was accomplished by HBr/CH_3COOH cleavage followed by acylation with p-nitrophenyl acetate. Yield of recrystallized IIIa = 28%; anal. calcd. for $C_{15}H_{27}O_5N_3$: C, 54.70%; H, 8.26%; N, 12.76%; found: C, 54.16%; H, 8.25%; N, 12.61%.

Yield of recrystallized IVa = 53%; anal. calcd. for $C_{19}H_{34}O_6N_4$: C, 55.05%; H, 8.27%; N, 13.52%; found: C, 54.86%; H, 8.41%; N, 13.56%.

Carbobenzoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyramide (IIIb). Ammonia was bubbled through a solution of 0.2 g III in 20 ml of methanol at 0°C for two hours. After standing at room temperature for 18 days, the solution was evaporated. Yield = 0.19 g (97.3%); anal. calcd. for $C_{20}H_{30}O_5N_4$: C, 59.10%; H, 7.44%; N, 13.78%; found: C, 59.25%; H, 7.48%; N, 13.69%.

Acetoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyramide (IVb) was prepared from IVa and ammonia. Yield ≅ ~100%; anal. calcd. for $C_{18}H_{33}O_5N_5$: C, 54.12%; H, 8.32%; N, 17.52%; found: C, 53.48%; H, 8.18%; N, 17.08%.

Acetoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyr-n-propyl-amide (IVc) was prepared from IVa by the above method except n-propylamine was used instead of ammonia. Yield: ≅ ~100%; anal. calcd. for $C_{21}H_{39}O_5N_5$: C, 57.12%; H, 8.90%; N, 15.86%; found: C, 56.46%; H, 8.84%; N, 15.26%.

Carbobenzoxy-γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyric acid (IIIc). Saponification of III with methanolic KOH at

room temperature, followed by filtration through cation exchange resin and evaporation of the neutral solution, gave a brown semisolid which showed traces of methoxy protons in the NMR. The analytical data of the solid agree fairly well with structure IIIc. Anal. calcd. for $C_{20}H_{29}O_6N_3$: C, 58.95%; H, 7.17%; N, 10.31%; acid no., 137.7 mg KOH/g; found: C, 56.82%; H, 6.35%; N, 9.01%; acid no., 157.7 mg KOH/g.

γ-aminobutyryl-γ-aminobutyryl-γ-aminobutyric acid (IIId). A solution of IIIb in 20 ml of 15% HBr in acetic acid was allowed to stand at room temperature. Ether was added, and the formed precipitate was dissolved in methanol. The methanol solution was filtered through an anion exchange resin and evaporated to yield a solid.

The NMR of the compound showed no methoxy, aromatic, or benzylic protons. Anal. Calcd. for $C_{12}H_{24}O_3N_4$: C, 52.92%; H, 8.88%; N, 20.57%; found: C, 47.31%; H, 7.86%; N, 17.21%.

Nylon 4 was prepared according to Reference 5 [$\eta sp/c$ = 7.8 dl/g (m-cresol, 25°C, 0.1 g/100 ml)].

Nylon 6 was prepared by the hydrolytic polymerization of epsilon-caprolactam at 255°C [$\eta sp/c$ = 0.62 dl/g (m-cresol, 25°C, 0.1 g/100 ml)].

Results and Discussion

Oligomers of γ-aminobutyric acid, bearing various end groups, were prepared by stepwise synthesis using the p-nitrophenyl active ester coupling method.[11] This technique has been pioneered by Bodanszky and was used with great success for the synthesis of complex, biologically active polypeptides.[12] In peptide chemistry, it is now well established that the p-nitrophenyl active ester route gives readily purifiable crystalline intermediates and virtually no side reactions.

The synthetic schemes leading to the various oligomers is summarized in Figure 1.

All of the compounds designated by Roman numerals are new compounds. The formulas and melting points of the synthesized oligomers are shown in Table I.

The thermal stability of the oligomers was investigated by thermal gravimetric analysis (TGA), both in isothermal operation and in the rising temperature mode. The results are summarized in Table II; for comparison TGA data of nylon 4, synthesized with a CO_2 catalyst,[5] and that of nylon 6 are also included.

FIGURE 1

SYNTHESIS OF END-CAPPED NYLON 4 OLIGOMERS

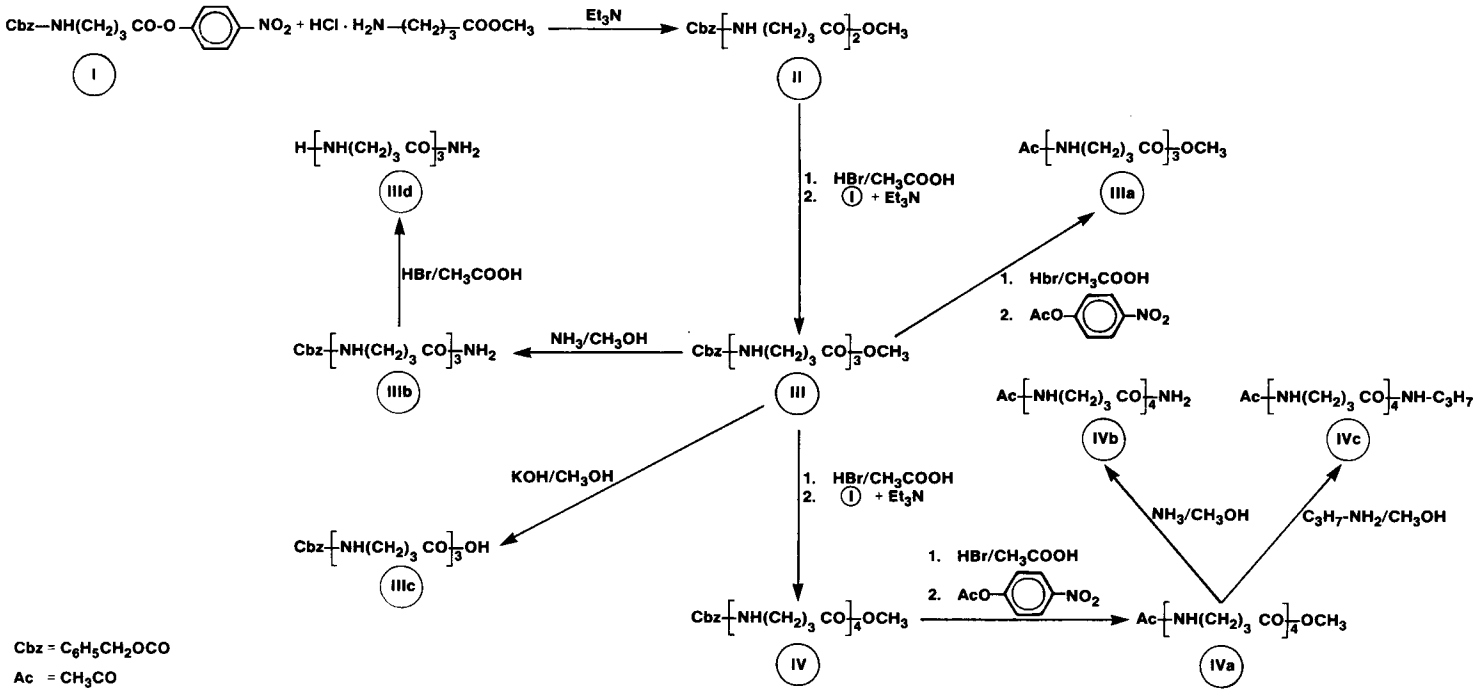

Table I

End-Capped Nylon 4 Oligomers

$X\text{—}[NH(CH_2)_3CO]_n\text{—}Y$

Compound	Formula	Mol Wt	X	Y	n	m.p., °C
I	$C_{18}H_{18}O_6N_2$	358.35	$C_6H_5CH_2OCO$	O-  -NO_2	1	82-82.5
II	$C_{17}H_{24}O_5N_2$	336.39	$C_6H_5CH_2OCO$	OCH_3	2	88.5-89
III	$C_{21}H_{31}O_6N_3$	421.50	$C_6H_5CH_2OCO$	OCH_3	3	139.5-140
IIIa	$C_{15}H_{27}O_5N_3$	329.41	CH_3CO	OCH_3	3	147-149
IIIb	$C_{20}H_{30}O_5N_4$	406.49	$C_6H_5CH_2OCO$	NH_2	3	200-202
IIIc	$C_{20}H_{29}O_6N_3$	407.47	$C_6H_5CH_2OCO$	OH	3	
IIId	$C_{12}H_{24}O_3N_4$	272.35	H	NH_2	3	138-144
IV	$C_{25}H_{38}O_7N_4$	506.61	$C_6H_5CH_2OCO$	OCH_3	4	173-175
IVa	$C_{19}H_{34}O_6N_4$	414.52	CH_3CO	OCH_3	4	177-178
IVb	$C_{18}H_{33}O_5N_5$	399.49	CH_3CO	NH_2	4	210-214
IVc	$C_{21}H_{39}O_5N_5$	441.57	CH_3CO	$NH\text{-}C_3H_7$	4	212-216

Table II

Isothermal and Rising Temperature TGA of End-Capped Nylon 4 Oligomers

$X\text{—}[NH(CH_2)_3CO]_n\text{—}Y$

Compound	n	X	Y	Weight Loss,[1] %	T_{50}, °C[2]
IIIa	3	CH_3CO	OCH_3	99	221
III	3	$C_6H_5CH_2OCO$	OCH_3	95	244
IIIc	3	$C_6H_5CH_2OCO$	OH	93	245
IIIb	3	$C_6H_5CH_2OCO$	NH_2	75	289
IIId	3	H	NH_2	92	268
IVa	4	CH_3CO	OCH_3	97	222
IV	4	$C_6H_5CH_2OCO$	OCH_3	96	254
IVb	4	CH_3CO	NH_2	97	281
IVc	4	CH_3CO	$NH\text{-}C_3H_7$	15	328
Nylon 4				22	308
Nylon 6				1.3	453

[1] 281°C, 10 minutes, N_2.

[2] Temperature at 50% weight loss; 10°C/minute, N_2.

The results of both TGA investigations show that the end-capped oligomers are thermally unstable, decomposing at temperatures close to the melting point of nylon 4. With the exception of the acetoxy- and propylamido-terminated tetramer (IVc), all of the oligomers investigated show poorer thermal stability than nylon 4 by TGA. This observation may be due to the fact that the lower molecular weight fragments formed from the oligomers volatilize more rapidly. By rising temperature TGA, it was found that the carboxamide-terminated compounds (IIIb, IVb, and IVc) are more stable than the other oligomers and undergo 50% weight loss at a higher temperature. The results of both series of TGA investigations clearly show that nylon 6 is considerably more stable than either nylon 4 or any of the oligomers examined in this study.

The thermal instability of the oligomers was confirmed by a gas chromatographic study of the decomposition reaction. In these experiments, the oligomer was dissolved in dimethyl sulfoxide and introduced into the gas chromatograph whose injection port was kept at 280°C. Under these conditions, the oligomers decompose instantaneously and yield pyrrolidone in near-quantitative yield. These results are summarized in Table III.

The conclusion which emerges from this investigation is that appropriate end capping may slow down the rate of thermal depolymerization of pyrrolidone oligomers. In the present

Table III

Decomposition of End-Capped Nylon 4 Oligomers in the Gas Chromatograph[1]

Compound	Compound Injected, Moles x 10^5	Pyrrolidone Formed, Moles x 10^5	Moles of Pyrrolidone / Moles of Compound
II	1.8	3.0	1.7
III	1.4	4.8	3.4
IV	1.2	4.9	4.1
IVa	1.5	5.4	3.6

[1]Ten percent solution in DMSO, epsilon-caprolactam internal standard, injector port: 280°C.

Programmed Carbowax 20M column: 100-200°C

study, the best thermal stability was obtained with Compound IVc where the acetoxy and n-propylamido end groups practically duplicate the structural elements of the main chain (almost a "no end group" situation). It is significant, however, that even IVc is considerably less stable than nylon 6. Therefore, it is reasonable to suggest that linear sequences of γ-aminobutyryl units are inherently unstable with a strong tendency to revert into the thermodynamically more stable pyrrolidone ring. The observed thermal instability of the nylon 4 oligomers is consistent with the reported small negative enthalpy of pyrrolidone polymerization.[13]

An extrapolation of these results to nylon 4 suggests that the high molecular weight polymer's thermal instability is also inherent in its structure which, however, may be somewhat modified by end groups, catalyst residues, branches, or "weak links."

References

1. L. Szego, La Chimica E L'Industria, 55, 280 (1973).
2. H. Sekiguchi, F. Carriere, and B. Coutin, Informations Chimie, No. 156, p 103 (1976).
3. K. Dachs and E. Schwartz, Angew. Chem., 74, 540 (1962).
4. E. M. Peters and J. A. Gervasi, Chemtech, p 16 January 1972.
5. C. E. Barnes, U.S. Patent 3,721,652 (1973).
6. H. Sekiguchi, P. Tsourkas, F. Carriere, and R. Audebert, European Polymer Journal, 10, 1185 (1974).
7. G. Bonta, A. Cifferi, and S. Russo, ACS Symposium, Series 59, 216 (1977).
8. Y. Wolman, D. Ladkany, and M. Frankel, J. Chem., Soc. (C), 689, (1967).
9. M. Brenner and W. Huber, Helv. Chim. Acta 36, 1109 (1953).
10. D. L. Garmaise, R. Schwartz, and A. F. McKay, J. Am. Chem. Soc., 80, 33 (1958).
11. M. Bodanszky and V. du Vigneaud, J. Am. Chem. Soc., 81, 5688 (1959).
12. M. Bodanszky and M. A. Ondetti, Peptide Synthesis, Interscience, New York, 1966.
13. O. Riedel and P. Wittmer, Makromol Chem., 97, 1 (1964).

Accepted December 7, 1983