Polymer Bulletin 13, 385–392 (1985)

Polymer Bulletin

Reaction of α, ω-Dicarboxy Polyamides in the Melt : Synthesis of a Model.

Use of N-Trifluoroacetylation in NMR and GPC Studies

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SUMMARY

The synthesis of N-dodecanoyl-11-aminoundecanoic acid as a model for carboxylic polyamides 11 is described. The solubilization reaction of these polyamides with trifluoroacetic anhydride is studied by ^{1}H and ^{13}C NMR spectroscopy. The resulting soluble trifluoroacetylated compounds are stable enough to allow an easy GPC study in CH_2Cl_2 on routine instument and columns. The participation of the residual dodecanoic acid in the polycondensation equilibrium of carboxylic polyamides has been established.

INTRODUCTION

The reaction between oligomers with functional end groups has been extensively used over the past few years for the synthesis of block polymers. The study of these reactions is difficult as they are usually carried out without solvents. When monofunctional models are available, they permit an easier determination of the experimental procedures of polycondensation between oligomers, and of the structure of resulting compounds.

The synthesis of models of carboxylic polyamides 11 is difficult as 11-aminoundecanoic acid polycondenses very easily. Moreover the low solubility of polyamides limits the possible methods of investigation, or imposes the use of expensive solvents (NMR and GPC in hexafluoroisopropanol) or equipment such as high temperature GPC.

Some authors recently described a method involving the N-trifluoroacetylation of high molecular weight polyamides (1,2) which allows their solubilization in low cost solvents at low temperatures, so that the NMR and GPC analysis can be carried out under usual conditions.

A study in our laboratory showed that this method can also be used for polyamides with reactive NH_2 end groups (3) .

This article reports the study of polyamides with carboxy end groups and of N-dodecanoyl-11-aminoundecanoic acid (DAUA) as a model.

SYNTHESIS OF N-DODECANOYL-11-AMINOUNDECANOIC ACID (DAUA)

The general techniques of polypeptide synthesis could be used here; however the following steps would be required :

- protection of amino group by trifluoroacetylation (4) or formation of N-carbobenzoxy derivatives (5,6), in order to avoid the polycondensation of 11-aminoundecanoic acid (AUA).

-protection of terminal carboxyl group by esterification with alcohols, such as benzyl alcohol(7), tbutanol(8), paranitrobenzyl alcohol(9), 4-sulfobenzyl alcohol(10), 1,1,1-trichloroethanol or a mixture of 1,1,1-trichloroethanol and 2-hydroxypyridine(11).

-deprotection of amino group by $NaBH_4$(12)

-reaction with dodecanoyl chloride

and, finaly, deprotection of carboxyl group.

Due to the number of steps necessary for this synthesis high yields cannot be expected. A direct condensation involving 11-aminoundecanoic acid and dodecanoic acid was carried out.

Two methods were investigated.

-stoichiometric reaction of dodecanoyl chloride in a suspension of 11-aminoundecanoic acid in N-methylpyrrolidone:

$$CH_3-(CH_2)_{10}-COCl + n\ NH_2-(CH_2)_{10}-COOH \xrightarrow[N(Et)_3]{} CH_3-(CH_2)_{10}(CNH-(CH_2)_{10})_n-COOH + HCl$$

triethylamine acting as an HCl and free carboxyl groups trap. Solvents were removed by washing the medium with water and higher oligomers free DAUA was obtained by extraction and crystallization. As this reaction leads to a mixture of oligomers with n=2,3,4 instead of pure n=1, we used the simplest possible method as follows:

-direct reaction of excess dodecanoic acid with 11-aminoundecanoic acid in the melt and azeotropic distillation of water with toluene. A mixture of compounds with n=1-5 was obtained; however it contained mainly DAUA (n=1) which could be extracted and crystallized as mentioned above.

TRIFLUOROACETYLATION OF CARBOXY MONOAMIDE AND POLYAMIDE 11

When a slight excess of trifluoroacetic anhydride is added to a suspension of DAUA or α-carboxy polyamide 11 in solvents such as CH_2Cl_2, $CHCl_3$, 1,2-dichloroethane a solubilization readily takes place, due to the N-acylation of amide groups in the chain and to the formation of anhydride on carboxy end groups which destroys intermolecular H-bonding

$$CH_3-(CH_2)_{10}-(C(=O)-N(-C(=O)CF_3)-(CH_2)_{10})_n-C(=O)-O-C(=O)-CF_3$$

The resulting solution is stable over 24h as long as contact with air moisture is avoided.

^{1}H NMR STUDY

The reaction is total as shown by the ^{1}H NMR spectrum of DAUA/TFA anhydride mixture (Fig. 1)

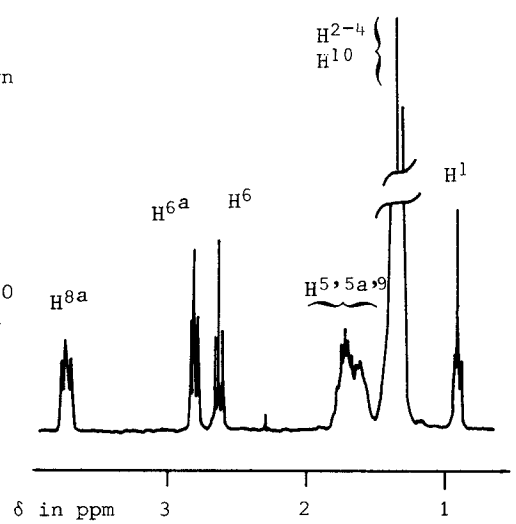


Fig. 1 - ^{1}H NMR spectrum ($CDCl_3$, 250 MHz, ref. TMS) of a mixture of DAUA and TFA anhydride (1/4 mol ratio).

(Same hydrogen numbering as carbons in Fig. 4B) .

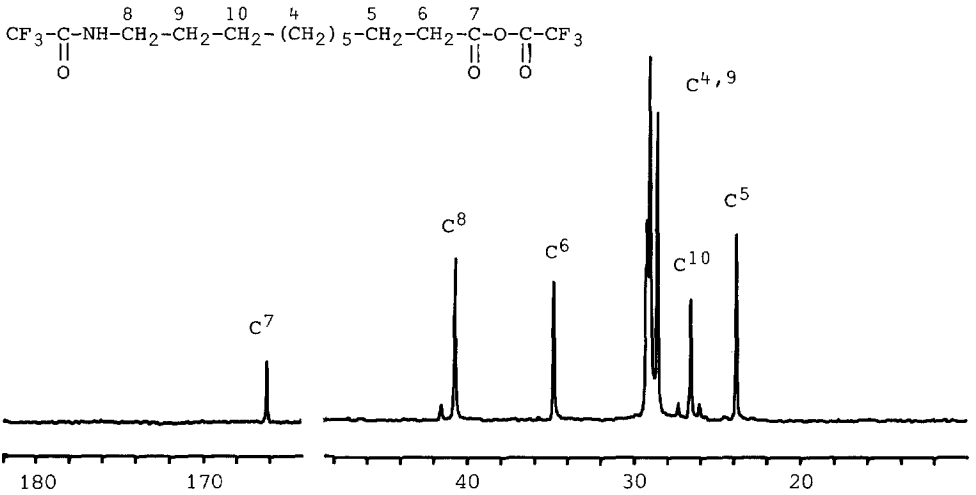
^{13}C NMR STUDY

Peaks assignments and numbering are reported in Figs.2-4 .

11-AMINOUNECANOIC ACID (AUA) (Fig.2)

Carbons close to the amino (C^8-C^{10}) and carboxy end groups (C^5-C^7) can be assigned by comparison with spectra of long chain acids and amines (13).

Small peaks close to these of C^8-C^{10} were thought to be due to the presence of a small amount of bis-trifluoroacetylated amino groups as similar peaks could be observed on dodecylamine/excess TFA anhydride mixture spectrum.



δ in ppm

Fig.2 - ^{13}C NMR spectrum ($CDCl_3$, 20.15 MHz, ref. $CDCl_3$=76.9 ppm) of a mixture of 11-aminoundecanoic acid and trifluoroacetic anhydride in 1/8 mole ratio.

DODECANOIC ACID (DA)

When dodecanoic acid is treated with excess trifluoroacetic anhydride its ^{13}C NMR spectrum (Fig. 3A) is close to the spectrum recorded without this anhydride.

It can easily be assigned by comparison with known spectra of similar compounds (13).

Only one difference is observed as the carbonyl peak is shielded from 180 to 166 ppm due to the formation of the following anhydride :

$CH_3-(CH_2)_{10}-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CF_3$

When TFA anhydride is not present in excess (Fig.3B) or when the solution is not freshly prepared (t = 1 week) a splitting of the carbonyl peak and of the peaks of carbons in α and β position to carbonyl carbons (C^5, C^6,C^7) is clearly observed . These peaks can be assigned to

$CH_3-(CH_2)_8-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{\underset{\underset{O}{\|}}{C}}-O-\underset{\underset{O}{\|}}{C}-CF_3$ $\quad$ $CH_3-(CH_2)_8-\overset{5'}{CH_2}-\overset{6'}{CH_2}-\overset{7'}{\underset{\underset{O}{\|}}{C}}-O-\underset{\underset{O}{\|}}{\overset{7'6'}{C}}-\overset{5'}{CH_2}-CH_2-(CH_2)_8-CH_3$

$CH_3-(CH_2)_8-\overset{5"}{CH_2}-\overset{6"}{CH_2}-\overset{7"}{COOH}$

An excess of TFA anhydride is therefore necessary in GPC studies to ensure that all carboxy end groups are converted to $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CF_3$ and that no chain coupling by anhydride groups takes place.

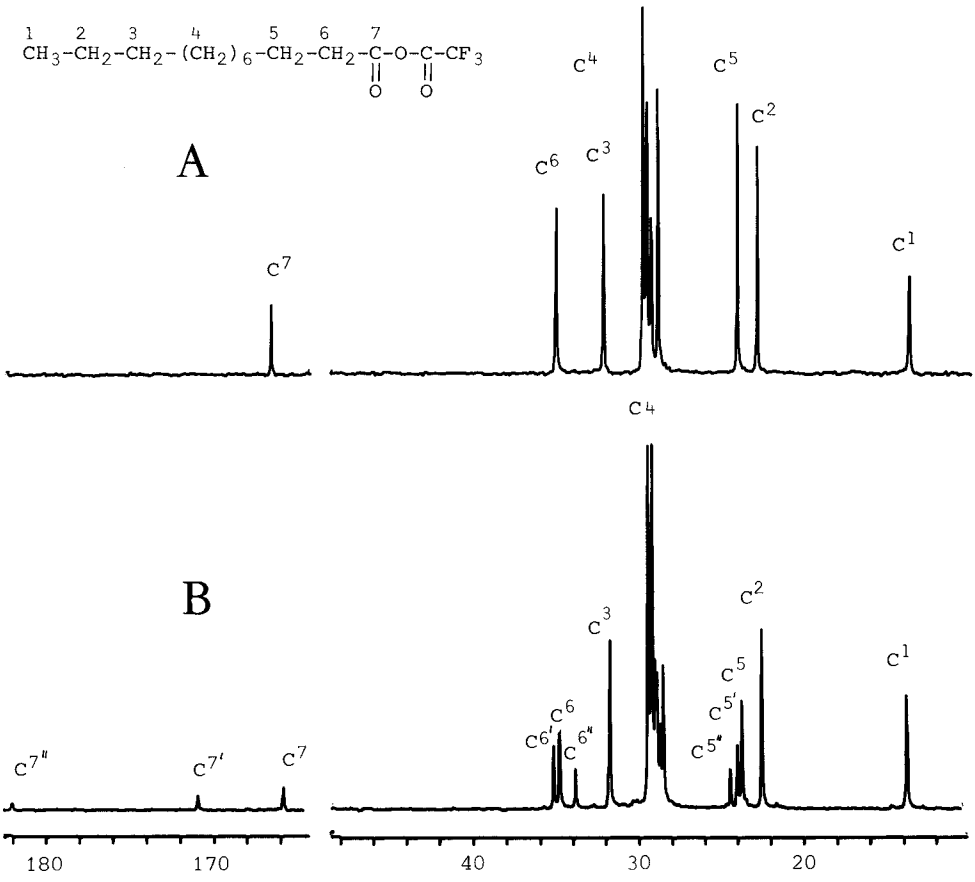
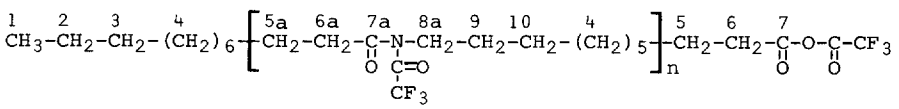


Fig.3 - ^{13}C NMR spectra ($CDCl_3$, 20.15 MHz, ref. $CDCl_3$=76.9 ppm) of mixtures of dodecanoic acid (DA) and trifluoroacetic anhydride (TFA-an).
A- 4/1 mol ratio TFA an/DA
B- 0.9/1 mol ratio TFA an/DA (For $C^{5'}$-$C^{7'}$ and $C^{5''}$-$C^{7''}$ see text)

N-DODECANOYL-11-AMINOUNDECANOIC ACID (DAUA) AND α-DODECYL ω-CARBOXY POLYAMIDE 11 (DCPA11)

Their spectra could be easily assigned by comparison with these of the above compounds. Due to the presence of amide groups new peaks appear. The corresponding carbons are referenced C^{5a}-C^{10a} (Fig.4). There is a long range coupling between C^{8a} and the fluorine atoms of trifluoromethyl groups, giving a quadruplet for the resonance of this carbon (J=2.2 Hz).



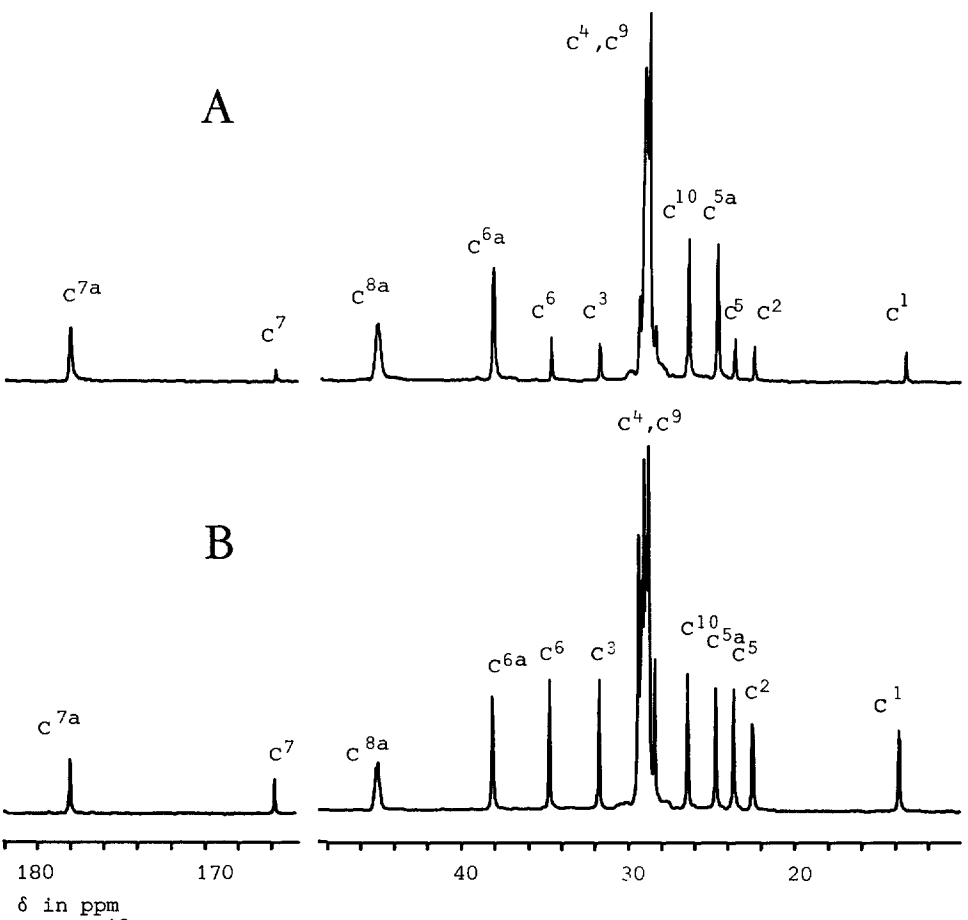


Fig.4 - ^{13}C NMR spectra ($CDCl_3$, 20.15 MHz, ref. $CDCl_3$=76.9 ppm) of mixtures of carboxylic oligoamides with excess trifluoroacetic anhydride (1mol/mol repeating unit + 2mol/mol oligomer)
A: α-carboxy polyamide 11 (DCPA11) Mn=1060, n=4.7
B: N-dodecanoyl-11-aminoundecanoic acid (DAUA) n=1

Exactly the same resonances are found for DAUA and DCPA 11, with lower intensities for end group carbons C^1- $C^3$and C^5- C^7 in DCPA 11 spectrum. This shows that DAUA is a good satisfactory model of oligomers with higher $\overline{DP}_n$.

Solutions with excess TFA-an have a good stability, as after 1 week storage in NMR tube, DAUA/TFA-an mixture gave a spectrum showing only minor changes, with the appearance of the low intensity peaks $C^{5'}$ - $C^{7'}$ and $C^{5''}$ - $C^{7''}$ already described for dodecanoic acid.

The GPC study of freshly prepared solutions of carboxylic oligoamides with excess trifluoroacetic anhydride can therefore be carried out.

GPC STUDY OF POLYAMIDIFICATION EQUILIBRIUM IN CARBOXYLIC POLYAMIDE-11.

When DAUA is heated to 180°C under nitrogen atmosphere, no loss of carboxyl grqups is observed up to t = 30 h. However the gas chromatography studies of the reaction medium showed the appearance of an increasing amount of dodecanoic acid with increasing reaction time, due to the polycondensation equilibrium between dodecanoic acid, DCPA 11 and DAUA.

$$D-(U)_m-COOH + D-(U)_{n-m}-COOH \rightleftharpoons D-COOH + D-(U)_n-COOH \qquad \begin{matrix} n=1,... \\ m=1,....,n \end{matrix}$$

$$D = CH_3-(CH_2)_{10}-$$

$$U = -\overset{\overset{O}{\|}}{C}-NH-(CH_2)_{10}-$$

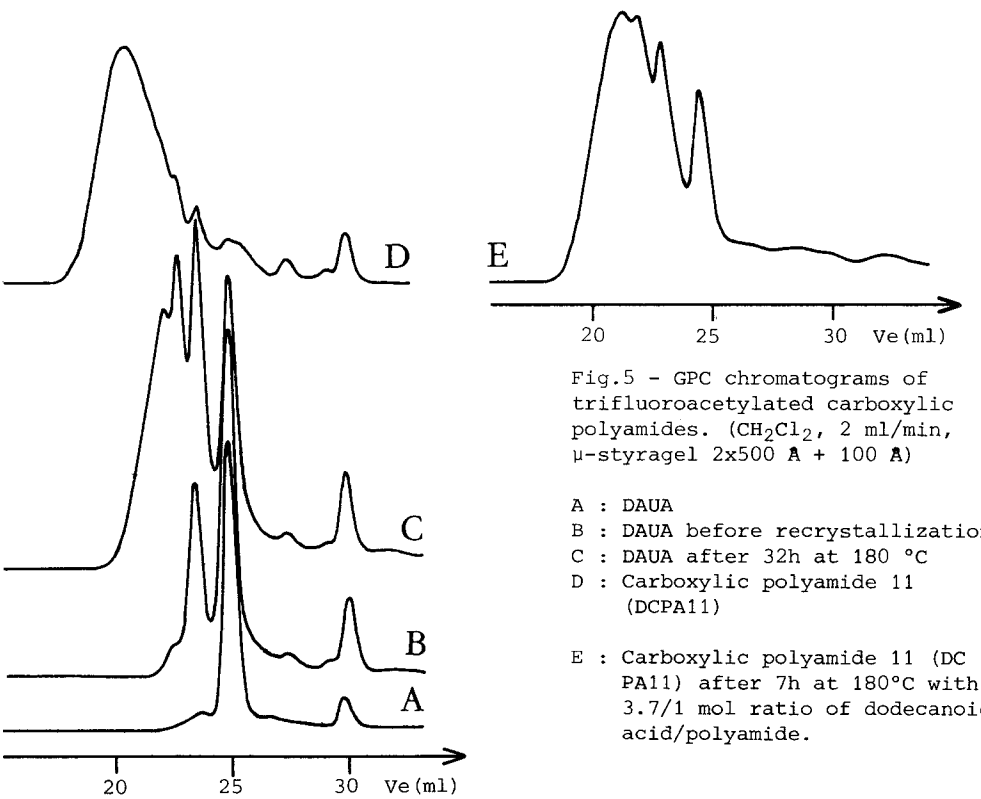


Fig.5 - GPC chromatograms of trifluoroacetylated carboxylic polyamides. (CH_2Cl_2, 2 ml/min, μ-styragel 2x500 Å + 100 Å)

A : DAUA
B : DAUA before recrystallization
C : DAUA after 32h at 180 °C
D : Carboxylic polyamide 11 (DCPA11)

E : Carboxylic polyamide 11 (DCPA11) after 7h at 180°C with 3.7/1 mol ratio of dodecanoic acid/polyamide.

GPC chromatograms recorded in CH_2Cl_2 after trifluoroacetylation showed that oligomerization of DAUA took place : oligomers up to n=4 were separated (Fig.5A-C). Dodecanoic acid appeared but it could be more clearly detected using gas chromatography. The same peaks can be found on the GPC chromatogram of α-dodecyl ω-carboxy polyamide 11 (DCPA11) (Fig.5D).

When DCPA11 is heated with dodecanoic acid the molecular weight decreases showing the reversibility of the reaction. (Fig.5E)

EXPERIMENTAL

Chemicals : Dodecanoic acid (Fluka, 99%), dodecanoyl chloride (Janssen, 98%), 11-aminoundecanoic acid (Fluka, 98+%), trifluoroacetic anhydride (Janssen, 99+%), N-methyl-2-pyrrolidone (Janssen, 99%), triethylamine (Prolabo) were used without further purification. α-dodecyl,ω-carboxy polyamide 11 was obtained from ATOCHEM (F) (Mn=1060).

N-dodecanoyl-11-aminoundecanoic acid (DAUA)

Reaction in solution : Dodecanoyl chloride (1 mol, 231 ml) was added dropwise at room temperature to a suspension of 11-aminoundecanoic acid (1 mol, 201g) in a mixture of triethylamine (4.4 mol, 320 ml) and N-methyl-2-pyrrolidone (2500 ml). The resulting mixture was then poured into 0.2N hydrochloric acid and the precipitate was filtered, washed with water, added to THF to form a suspension. The higher oligomers were filtered off, THF evaporated at room temperature and the residue recrystallized in methylethylketone.

Reaction in the melt : A stoichiometric mixture of dodecanoic acid and 11-aminoundecanoic acid was heated with 10% wt toluene in a flask equipped with a Dean Stark separator until the azeotropic distillation of reaction water (85°C) was completed. The reaction medium was then treated with THF as above, and DAUA recrystallized in methylethylketone.

Study of polyamidification equilibrium

Oligomerization of N-dodecanoyl-11-aminoundecanoic acid (DAUA): DAUA was maintained at 180°C for 32h under nitrogen, then trifluoroacetylated (see below) and analyzed by GPC

Depolyamidification of carboxylic polyamide 11 (DCPA11) : A mixture of DCPA11 and dodecanoic acid (1/3.7 mol ratio) was heated to 180°C for 7h under nitrogen then analyzed by GPC after trifluoroacetylation.

GPC

Chromatograms were recorded on a Waters apparatus (6000A pump, U6K injector, R401 refractometric detector) with a Kratos Spectroflow 757 UV detector at 230 nm . A 2x500 Å + 100 Å μ-styragel column set was used with a 2 cm^3/min flow rate of dichloromethane (Carlo-Erba, HPLC grade).

Sample preparation : ca. 5mg of the compound to be analyzed was suspended or dissolved in dichloromethane, and an excess of trifluoroacetic anhydride was added. The resulting solution was allowed to stand 1h at room temperature before injection.

NMR spectroscopy

Spectra were recorded on Bruker 80FT and 250FT spectrometers. Samples were dissolved or suspended in $CDCl_3$ and excess trifluoroacetic anhydride was added. (See Figs. 1-4 for mol ratios).

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Accepted April 2, 1985