Bull Soc Chim Fr (1995) 132, 967-974

Study of dimerization and polymerization of *N*-alkylcyanoacetamides

Hélène Migeon, Alain Fradet, Pierre-Jean Madec, Ernest Maréchal*

Laboratoire de synthèse macromoléculaire, CNRS, URA 24,
Université Pierre-et-Marie-Curie, 4, place Jussieu, 75252 Paris Cedex 05, France

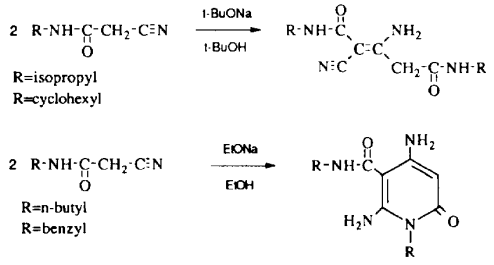
(received 11 May 1995, accepted 20 July 1995)

Summary – The solution and bulk dimerization of *N*-alkylcyanoacetamides has been studied in the presence of bases using ^{1}H and ^{13}C NMR, IR spectroscopy and SEC. The influence of catalysts has been investigated. The reaction proceeds in two steps: (i) formation of an enaminonitrile dimer by the Thorpe reaction; and (ii) intramolecular cyclization of this dimer to a substituted pyridinone. A reaction mechanism is proposed. The application of this reaction to a difunctional compound, *N*,*N*′-dodecamethylene-bis(cyanoacetamide), yielded polymers either in solution or in the bulk. Polymers with $\overline{M_n} \approx 12\,000$ were obtained.

N-alkylcyanoacetamide / Thorpe reaction / N,N′-dodecamethylene-bis(cyanoacetamide) polymerization / end group dimerization

Introduction

N-Alkylcyanoacetamides dimerize in the presence of strong bases [1] by a Thorpe reaction [2-4] giving enaminonitrile dimers. In some cases, these dimers undergo an intramolecular cyclization, leading to pyridinones (scheme 1).



Scheme 1

The application of this reaction to the chain extension of oligomers by end-group dimerization in the bulk should be an interesting way to avoid problems connected to by-product elimination and stoichiometry. This new step-growth polymerization method seems particularly suited to the preparation of block copolymers, starting from mixtures of oligomers with cyanoacetamido (A) end groups (reaction [1]).

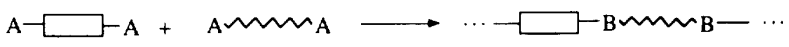
The Thorpe reaction has often been used on nitriles and dinitriles [2-6], but there is only one report concerning *N*-alkylcyanoacetamides [1]. The formation of enaminonitrile and the intramolecular cyclization to pyridinone are therefore still poorly known and the choice of catalyst and experimental conditions have not been optimized. Moreover, this reaction has never been carried out in the bulk or applied to the synthesis of polymers.

This article deals with the dimerization and polymerization of *N*-dodecylcyanoacetamide **1** and *N*,*N*′-dodecamethylene-bis(cyanoacetamide) **3**, respectively, as a first step toward the evaluation of this method.

Experimental section

Chemicals

Dodecylamine (Aldrich, 99%), ethyl cyanoacetate (Aldrich, 99%), hexane (SDS, 95%), ethanol (Prolabo, 99.8%), sodium (Prolabo, 98.7% in paraffin oil), acetonitrile (SDS, 99.7%), toluene (Prolabo, 99.5%), potassium *tert*-butoxide (Janssen, 95%), sodium methoxide (Aldrich, 95%), 4-(dimethylamino)pyridine (Aldrich, 99%), *N*-sodiohexamethyldisilazane (Aldrich, 98%) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (Aldrich, 98%) were used without further purification. Dodecamethylene diamine (Aldrich, 98%) was recrystallized in hexane. Sodium benzyloxide was synthesized from benzyl alcohol (Aldrich, 99%) and Na.



[1]

* Correspondence and reprints

Syntheses

• *Synthesis of* N-*dodecylcyanoacetamide* **1**

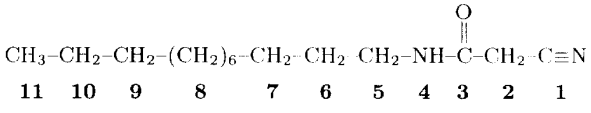
The procedure described by Renner *et al* [7] was applied to dodecylamine. Dodecylamine (59 g; 0.319 mol) and ethyl cyanoacetate (43 g; 0.38 mol) were placed in a 250 mL three-neck round-bottomed flask fitted with a distilling column and a nitrogen inlet and outlet. The mixture was heated to 160–180 °C under a nitrogen atmosphere. Ethanol was distilled off. After ethanol distillation, the medium was cooled to 110 °C and poured into 1 L of vigorously stirred *n*-hexane cooled in a water-ice bath. After filtration, **1** was recrystallized in hexane, and then in ethanol, giving white needles, which were dried at 50 °C under vacuum.

Yield: 95%.

$C_{15}H_{28}N_2O$: calc (%) C 71.43; H 11.11; N 11.11; O 6.35. Found (%) C 71.6; H 11.0; N 11.2; O 6.8.

M = 252 g mol^{-1} (MS); T_m = 90.5 °C; $T_{5\%}$ = 238 °C (5% mass loss at 20 °C min^{-1} heating rate).

IR (KBr): ν (cm^{-1}) = 3 303 (NH); 2 265 (C≡N); 1 663 (C=O).



^{1}H NMR (DMSO-d_6): δ (ppm) = 0.85 (t, H^{11}); 1.25 (H^7-H^{10}); 1.4 (m, H^6); 3.0 (q, H^5); 3.55 (s, H^2); 8.15 (t, H^4).

^{13}C NMR (DMSO-d_6): δ (ppm) = 13.55 (C^{11}); 21.8 (C^{10}); 25 (C^2); 26.1 (C^7); 28.5 (C^6, C^8); 31 (C^9); 40 (C^5); 115.7 (C^1); 161.4 (C^3).

• *Solution dimerization of* **1**: *synthesis of 2,4-diamino-N,1-didodecyl-6-oxo-1,6-dihydropyridine-3-carboxamide* **2a**

In a 250 mL three-neck round-bottomed flask fitted with a reflux column and nitrogen inlet and outlet, 10.08 g of **1** (40 mmol) was dissolved in a solution of 0.19 g Na (8.26 mmol) in 80 mL ethanol. The mixture was heated to reflux for 2 h. The solution was then poured in 2 L ice-water. After filtration, **2a** was washed with water several times until the filtrate was neutral. The white powder was then dried at 50 °C under vacuum. Yield: 89%. For analytical purposes, **2a** was recrystallized in acetonitrile and twice in ethanol.

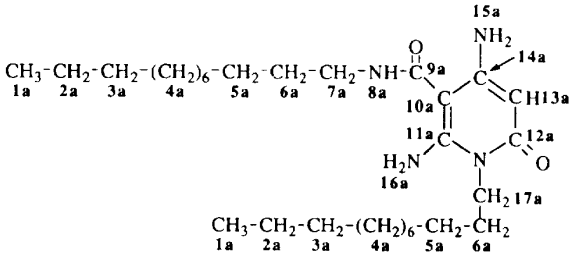
$C_{30}H_{56}N_4O_2$: calc (%) C 71.43; H 11.11; N 11.11; O 6.35. Found (%) C 71.2; H 10.9; N 11.2; O 6.3.

M = 504 g mol^{-1} (MS); T_m = 138 °C.

$T_{5\%}$ = 267 °C (5% mass loss at 20 °C min^{-1} heating rate).

IR (KBr): ν (cm^{-1}) = 3 452 and 3 386 (NH_2); 3 386 (NH_2); 3 306 (NH); 1 679 (CO); 1 621 (C=C).

^{1}H NMR (DMSO-d_6): δ (ppm) = 0.85 (t, H^{1a}); 1.25 (H^{2a}-H^{5a}); 1.4 (m, H^{6a}); 3.14 (q, H^{7a}); 3.8 (t, H^{17a}); 4.85 (s, H^{13a}); 5.66 and 7.02 (H^{15a}, H^{16a}); 7.58 (H^{8a}).



^{13}C NMR (DMSO-d_6): δ (ppm) = 13.55 (C^{1a}); 21.8 (C^{2a}); 26.1 (C^{5a}); 28.5 (C^{4a}, C^{6a}); 31 (C^{3a}); 40 (C^{7a}, C^{17a}); 84.65 (C^{10a}); 85.2 (C^{13a}); 152.1 (C^{14a}); 154.7 (C^{11a}); 160.1 (C^{9a}); 167 (C^{12a}).

• *Bulk dimerization of* **1**

Compound **1** (10 g, 39.7 mmol) and the chosen catalyst (0.5–2% weight) were placed in a 50 mL reactor equipped with a mechanical stirrer and nitrogen inlet and outlet. The reactor was immersed for 1 h in an oil bath at 150 °C. The orange solid obtained after cooling was analyzed without further purification.

• *Synthesis of 3-amino-2-cyano-*N,N′*-didodecylpent-2-enediamide* **2b**

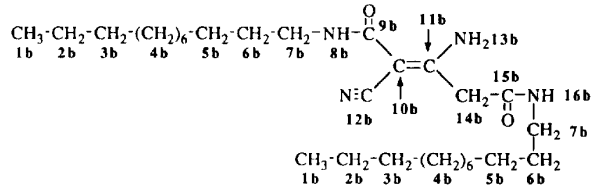
Compound **1** (10 g; 39.7 mmol) and *t*-BuOK (0.2 g; 1.78 mmol) were mixed in a 50 mL reactor fitted with nitrogen inlet and outlet. The reactor was immersed without stirring for 5 min in a preheated oil bath at 120 °C. It was then rapidly cooled in a water-ice bath. Thus the formation of the heterocyclic dimer was avoided. The obtained solid was recrystallized in 200 mL acetonitrile. The obtained powder was dissolved in 500 mL hot acetonitrile and the solution was slowly cooled to 30 °C. After filtration, the white powder was recrystallized in ethanol, and then dried at 50 °C under vacuum. Yield: 10%.

$C_{30}H_{56}N_4O_2$: calc (%) C 71.43; H 11.11; N 11.11; O 6.35. Found (%) C 70.9; H 11.2; N 11.0; O 6.6.

M = 504 g mol^{-1} (MS); T_m = 113.8 °C.

$T_{5\%}$ = 300 °C (5% mass loss at 20 °C min^{-1} heating rate).

IR (KBr): ν (cm^{-1}) = 3 411 and 3 359 (NH_2); 3 324 (NH); 2 192 (C≡N); 1 675 (C=O); 1 622 (C=C).



^{1}H NMR ($CDCl_3$): δ (ppm) = 0.87 (t, H^{1b}); 1.25 (H^{2b}-H^{5b}); 1.5 (m, H^{6b}); 3.23 (m, H^{7b}); 3.34 (s, H^{14b}); 5.78, 6.06, 7.47 and 9.95 (H^{8b}, H^{16b}, H^{13b}).

^{13}C NMR (DMSO-d_6): δ (ppm) = 13.55 (C^{1b}); 21.8 (C^{2b}); 26.1 (C^{5b}); 28.5 (C^{4b}, C^{6b}); 31 (C^{3b}); 39.4 (C^{14b}); 40 (C^{7b}); 71.4 (C^{10b}); 119.15 (C^{12b}); 164.8 (C^{11b}); 165.35 and 166.4 (C^{9b}, C^{15b}).

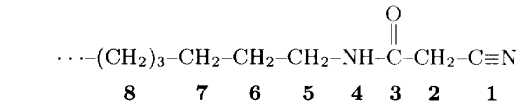
• *Synthesis of* N,N′*-dodecamethylene-bis(cyanoacetamide)* **3**

The procedure was the same as above (synthesis of **1**), with dodecane-1,12-diamine (50 g; 0.25 mol) and ethyl cyanoacetate (62.8 g; 0.556 mol). The hot mixture was poured into 500 mL EtOH. The powder obtained after filtration (80 g) was recrystallized in ethanol, dried under vacuum and recrystallized in toluene. Yield: 75%. A small amount of dimer (< 5%) was still present in the recrystallized product, which was used without further purification for the polymerization study.

$C_{18}H_{30}N_4O_2$: calc (%) C 64.67; H 8.98; N 16.77; O 9.58. Found (%) C 64.4; H 9.2; N 16.7; O 9.8.

M = 334 g mol^{-1} (MS); T_m = 141.5 °C; $T_{5\%}$ = 330 °C (5% mass loss at 20 °C min^{-1} heating rate).

IR (KBr): ν (cm^{-1}) = 3 324 (NH); 2 265 (C≡N); 2 199 (C≡N enaminonitrile); 1 663 (CO).



^1H NMR (DMSO-d_6): δ (ppm) = 1.2 (H^7, H^8); 1.35 (m, H^6); 3 (q, H^5); 3.53 (s, H^2); 8.12 (H^4).

^{13}C NMR (DMSO-d_6): δ (ppm) = 25 (C^2); 26.1 (C^7); 28.8 (C^6, C^8); 39 (C^5); 115.9 (C^1); 161.6 (C^3).

• *Solution polymerization of* **3** *by end-group dimerization*

The procedure was the same as above (synthesis of **2a**), with **3** (10 g; 30 mmol), and Na (0.3 g; 13 mmol) in 220 mL EtOH. After a 4 h reflux, half of the ethanol was distilled off, and the mixture was poured in 2 L ice-water. The white product was filtered, washed several times with water and then dried under vacuum.

$C_{18}H_{30}N_4O_2$: calc (%) C 64.67; H 8.98; N 16.77; O 9.58. Found (%) C 65.0; H 8.9; N 16.6; O 9.5.

• *Bulk polymerization of* **3**

The procedure was the same as that used for the bulk dimerization of **1**.

For the experiment with 2% *t*-BuOK, 1 h, 160 °C: Found (%) C 64.5; H 9.1; N 16.9; O 9.5.

Analytical methods

• *Infrared spectroscopy (FTIR)*

Fourier-transform infrared absorption spectra were recorded on a Bruker IFS 45 spectrometer. Solids were analyzed in KBr pellets and liquids in KBr cells.

• *Nuclear magnetic resonance (NMR)*

^1H NMR and ^{13}C NMR spectra were recorded on Bruker WM250 and AC200 spectrometers. In order to assign the class of carbon atom, DEPT and QUATD selective pulse sequences were used for ^{13}C NMR. Assignments were done using selective homo- and heteronuclear irradiations.

• *Size exclusion chromatography (SEC)*

Chromatograms were recorded on a Waters equipment (510 pump, U6K injector) using refractometric detection (Waters RI410), two 60 cm PL-Gel columns (5 μm particle size, 50 + 100 Å porosity) in THF (0.8 mL min^{-1}) and polystyrene calibration.

• *Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)*

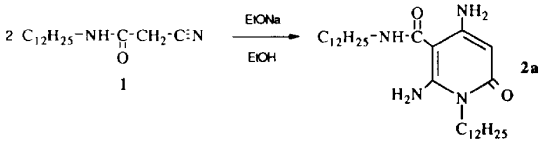
Analyses were carried out under nitrogen on a DuPont Instruments 9900 apparatus equipped with DSC910 and TGA951 modules at a heating rate of 20 °C min^{-1}. Glass transition temperatures (Tg) were measured from the second-heating curves.

Results and discussion

Dimerization of N-dodecylcyanoacetamide **1**

• *Solution dimerization*

The reaction was carried out according to Schmitz and Schramm [1] in ethanol in the presence of sodium ethoxide as a catalyst. Mass spectrometry shows that dimerization took place, since the compound obtained after recrystallization has a molar mass exactly double that of starting **1** (504 g mol^{-1}). The IR spectrum does not exhibit the nitrile band between 2 165 and 2 200 cm^{-1} characteristic of enaminonitrile dimer [8, 9]. The nitrile band of **1** at 2 265 cm^{-1} is no longer present, while a double band near 3 450 cm^{-1}, typical of NH_2 groups, and a band at 1 620 cm^{-1} assigned to C=C are present. This is consistent with the formation of heterocyclic dimer **2a** (scheme 2):



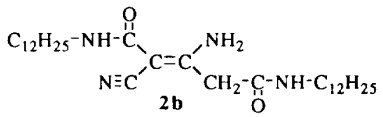
Scheme 2

This was confirmed by an NMR study. The ^1H NMR spectrum exhibits the peaks expected for **2a** (fig 1). The triplet at 3.8 ppm is assigned to methylene α to pyridinone nitrogen, and the singlet at 4.85 ppm to pyridinone CH. The peak at 7.5 ppm is assigned to an NH proton, coupled to the methylene at 3.1 ppm, as shown by homonuclear decoupling. ^{13}C NMR spectrum (fig 2) also fits structure **2a**. There is no peak in the 115–120 ppm region, which would be representative of nitriles, therefore of enaminonitrile dimer. Five quaternary carbons, at 84.7, 152.1, 154.7, 160 and 167 ppm, and a CH at 85.2 ppm appear instead, corresponding to structure **2a**.

• *Bulk dimerization*

The compound obtained after 1 h of reaction of **1** at 150 °C, in the presence of 2% potassium *t*-butoxide (*t*-BuOK) has been analyzed. The IR spectrum displays the same features as that of **2a**. The ^1H and ^{13}C NMR spectra are identical to those of cyclic dimer **2a** obtained by solution dimerization. Since no peak relative to **1** can be detected, the conversion is quantitative.

The reaction was monitored by SEC (fig 3). After 2 min reaction, a compound referred to as **2b** appeared. The main compound, **2a**, only appeared afterward, together with a small amount of a compound denoted **2c**. After 10 min reaction, almost all monomer **1** has disappeared. Compound **2b** was isolated and shown to be the enaminonitrile dimer by IR spectroscopy (strong C≡N absorption at 2 192 cm^{-1}) and mass spectrometry (molar mass is equal to that of **2a**).



The ^1H NMR spectrum of **2b** also fits the expected structure (see *Experimental section*). However, four signals of relative intensities 1:1:1:1 in the 5.5–10 ppm region remain unassigned, whereas only three peaks of relative intensities 1:1:2 (2 NH and 1 NH_2) are expected.

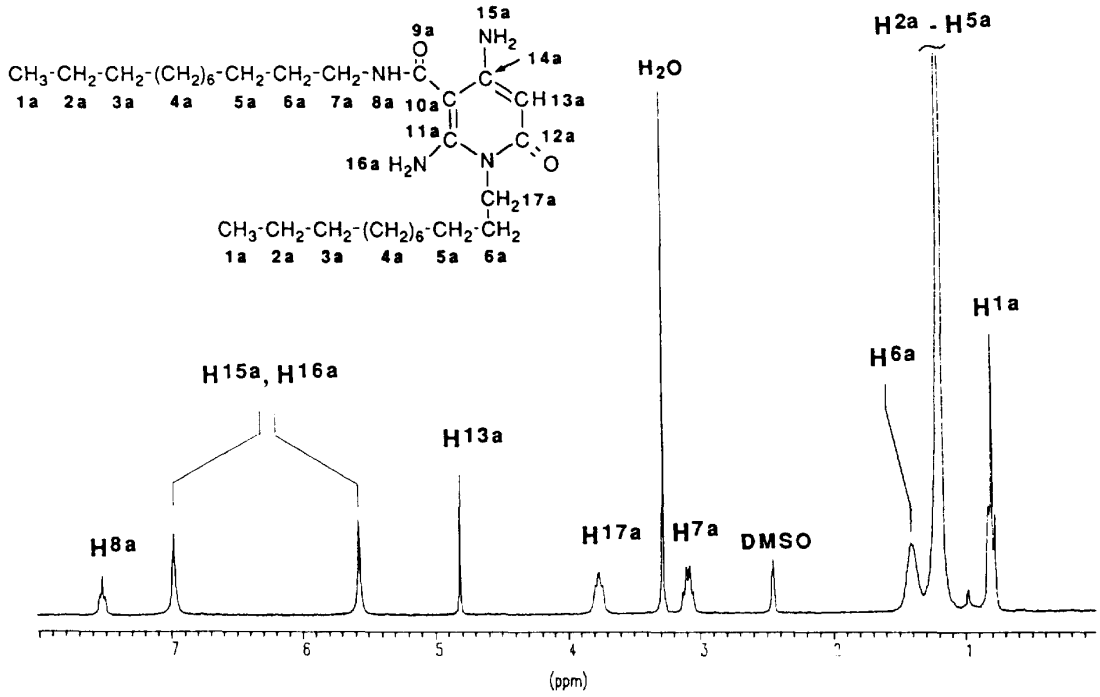


Fig 1. ^{1}H NMR spectrum of **2a** (250 MHz, DMSO-d_6, ref TMS).

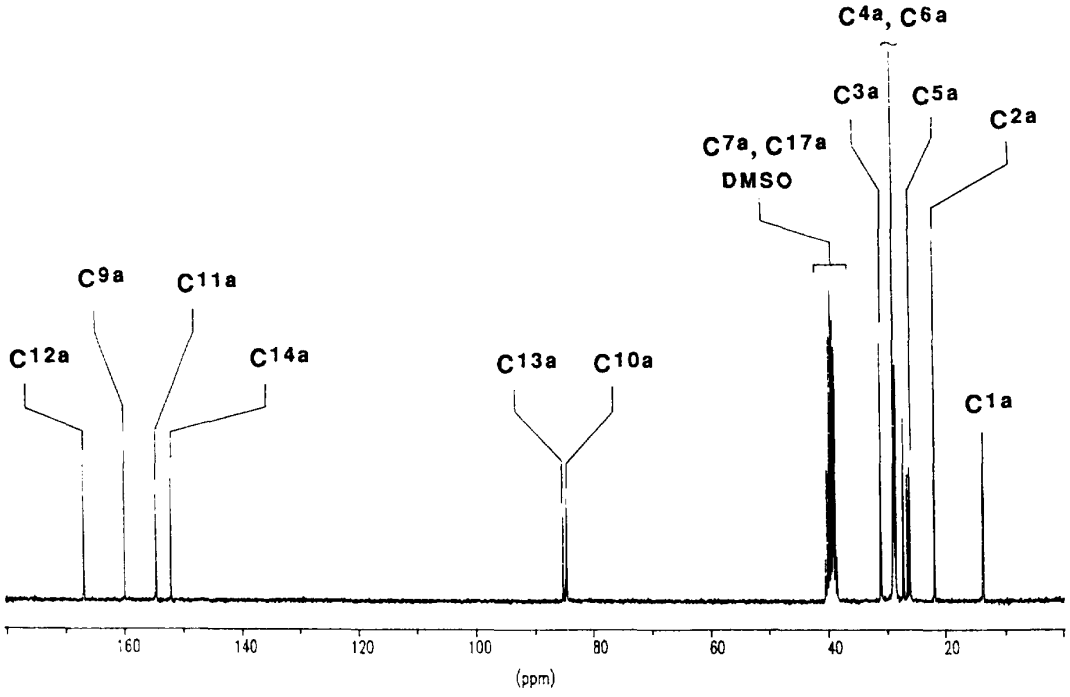


Fig 2. ^{13}C NMR spectrum of **2a** (62.9 MHz, DMSO-d_6, ref TMS). See figure 1 for C numbering.

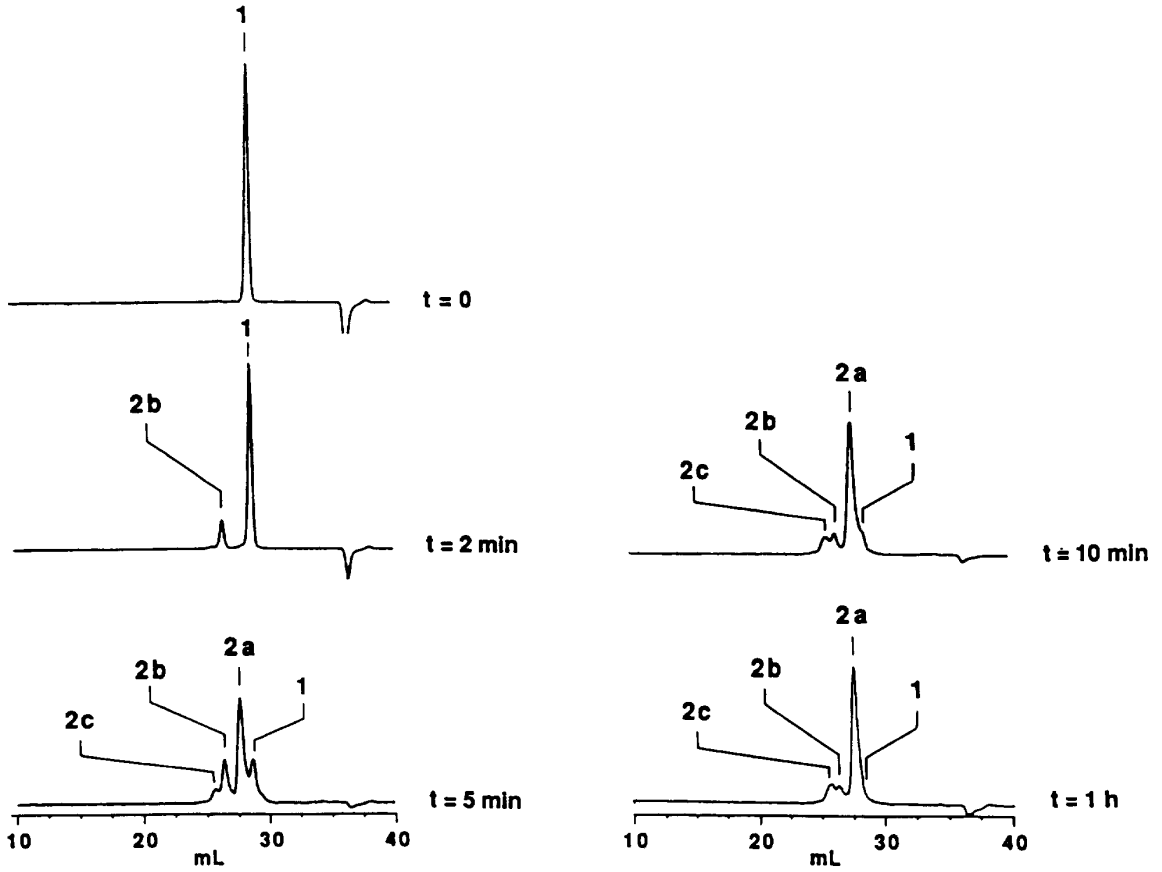
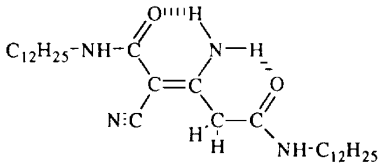


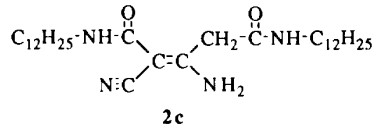
Fig 3. Bulk dimerization of **1** at 150 °C in the presence of 2% *t*-BuOK: SEC of the products obtained at various reaction times.

This might be due to an intramolecular H-bonding in the *E* isomer, leading to non-equivalence of amine protons:



The ^{13}C NMR spectrum also presents the features expected for **2b** (fig 4). Five quaternary carbon are assigned: *C*=O at 165.35 and 166.4 ppm, =*C*-NH_2 at 164.8 ppm, *C*≡N of enaminonitrile at 119.15 ppm and =*C*-CN at 71.4 ppm. None of the peaks are split. This confirms that **2b** is not a mixture of *E* and *Z* isomers, but probably only the *E* isomer.

Compound **2c** could not be isolated, and therefore its structure cannot be unambiguously determined. However, the mass spectrum of **2a–c** mixture does not exhibit any peak corresponding to masses higher than that of a dimer of **1**. IR and NMR spectra do not reflect any formation of compounds other than **1** dimers. **2c** can therefore reasonably be supposed to be the *Z* isomer:



2c

The following reaction scheme can be put forward for the dimerization of *N*-dodecylcyanoacetamide: (i) formation of enaminonitrile dimers **2b** and **2c** by the Thorpe reaction; and (ii) cyclization of **2b** to heterocyclic dimer **2a**. It must be noted that *Z* dimer **2c** cannot undergo cyclization (scheme 3).

From this mechanism, it is easy to understand why Schmitz and Schramm [1] did not obtain heterocyclic dimers for bulky R groups, since these hinder intramolecular cyclization.

• *Influence of catalyst*

Various basic catalysts have been compared: potassium *t*-butoxide (*t*-BuOK), sodium methoxide (MeONa), sodium benzyloxide (BZ: $C_6H_5CH_2ONa$), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-(dimethylamino) pyridine (DMAP), and *N*-sodiohexamethyldisilazane (SHDS). SHDS gives good results for the Thorpe–Ziegler cyclizations of dinitriles [10]. The raw products obtained after 1 h reaction at 150 °C with or without 2% (weight) catalyst have been studied by SEC. Conver-

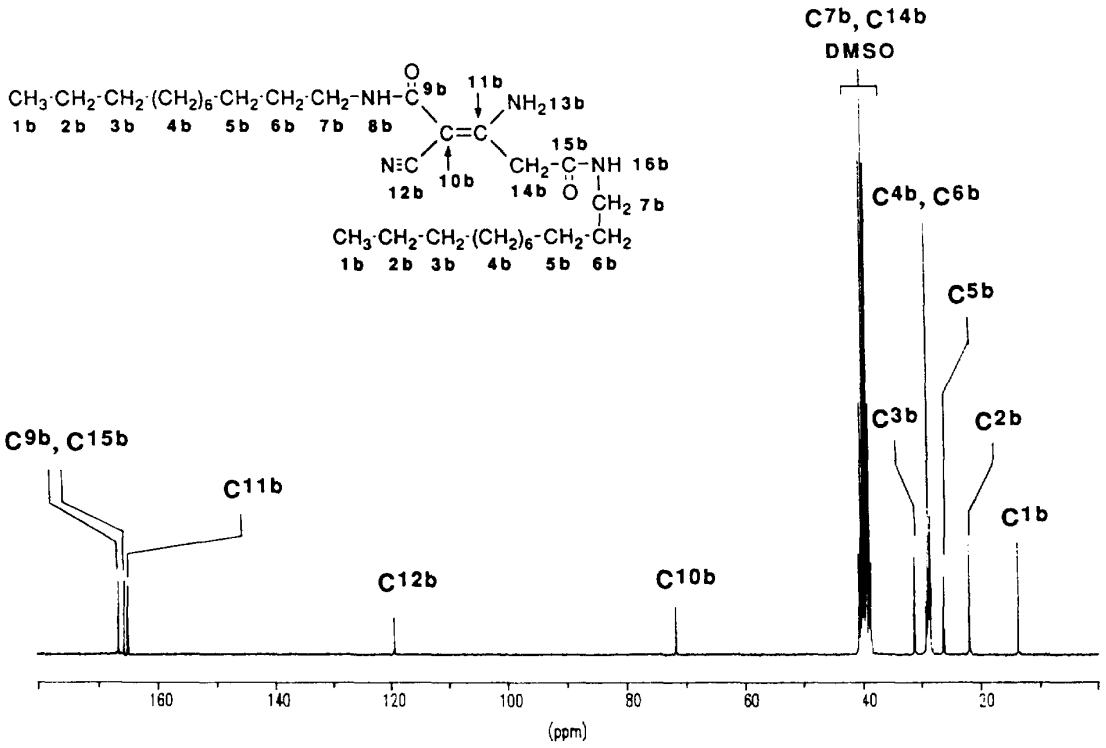
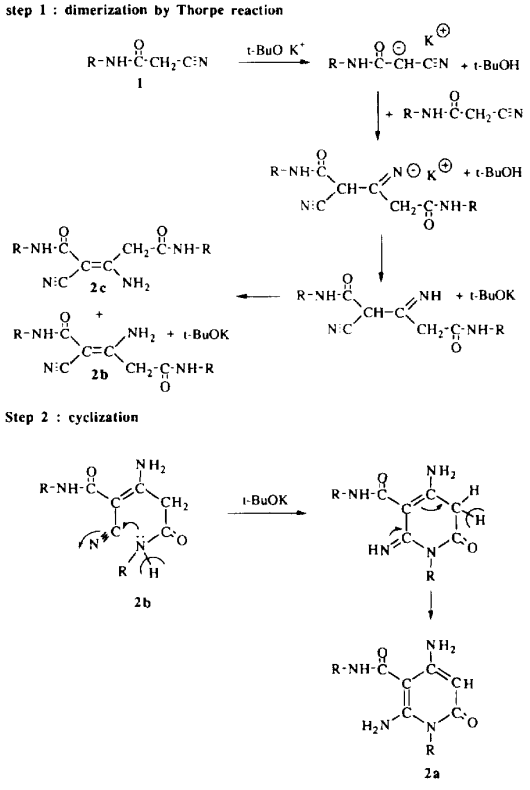


Fig 4. ^{13}C NMR spectrum of **2b** (62.9 MHz, DMSO-d_6, ref TMS).



Scheme 3

sions into **1**, calculated from SEC chromatograms and a calibration curve, are reported in table I. Dimerization does not take place in the absence of a catalyst or with DMAP. The strongest base (*t*-BuOK) leads to the highest conversion. Catalyst basicity is therefore an important factor of the reaction. DBU is a strong base, but only low conversions were obtained, due to its evaporation from the reaction medium at 150 °C. No other secondary reaction other than a slight release of NH_3 was observed during dimerization. This release takes place when the amount of catalyst is high (> 2%), and may be explained by a condensation between amine moieties.

Table I. Bulk dimerization of **1** in the presence of various catalysts (2% weight): fractional conversion after 1 h reaction at 150 °C. (MeONa = sodium methoxide, BZ = sodium benzyloxide, *t*-BuOK = potassium *t*-butoxide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, SHDS = *N*-sodiohexamethyldisilazane, DMAP = 4-(dimethylamino)pyridine).

Catalyst	None	MeONa	BZ	*t*-BuOK	DBU	SHDS	DMAP
Conversion	0	0.90	0.82	1.00	0.66	0.90	0

Polymerization of N,N′-*dodecamethylene-bis(cyanoacetamide)* **3**

During the synthesis of **3** by reaction between dodecane-1,12-diamine and ethyl cyanoacetate, some polymerization already takes place. A weak enaminonitrile band is observed in the spectra and a small amount of dimer

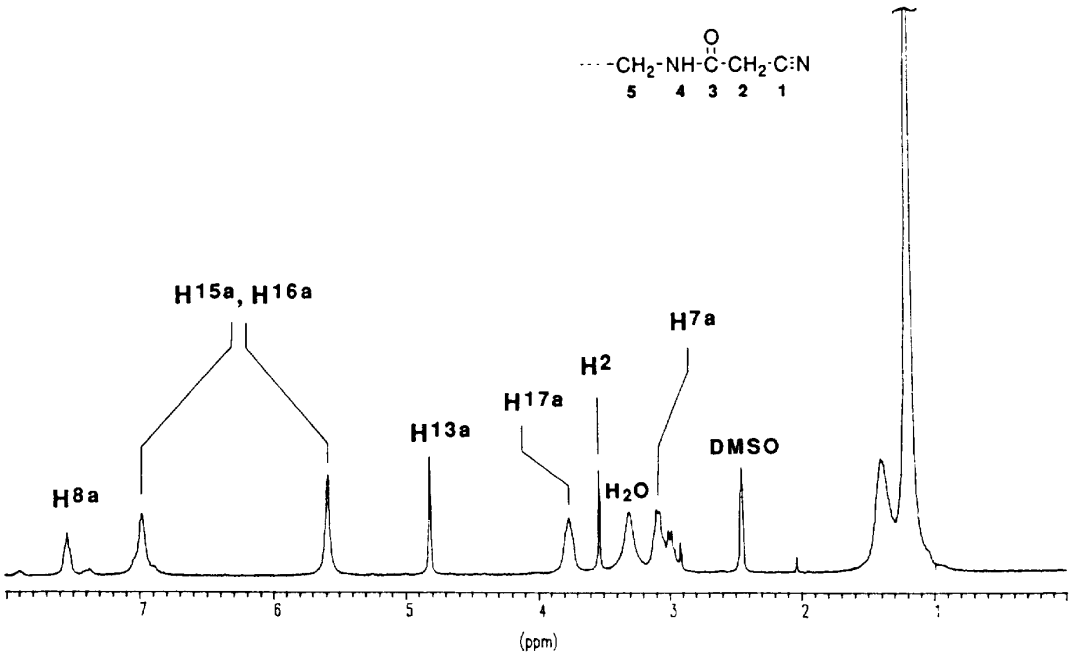
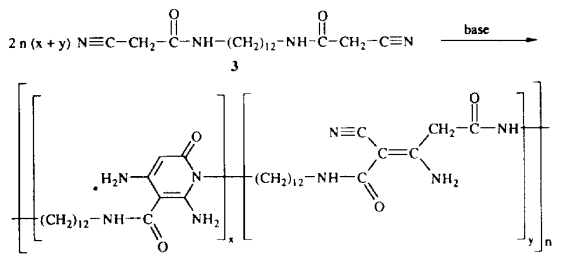


Fig 5. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, ref TMS) of the polymer obtained by solution polymerization of **3** in EtONa/EtOH. See figure 1 for H numbering.

(less than 5%) is detected in SEC chromatograms. As cyanoacetamide group dimerization can lead either to substituted pyridinone or enaminonitrile moieties, the step growth polymerization of **3** can be written as follows (scheme 4):



Scheme 4

• *Solution polymerization*

The IR spectrum of the compound obtained after reaction in ethanol and precipitation in water shows that reaction has taken place. The intensity of C≡N band at 2 265 cm^{-1} has strongly decreased and the weak band at 2 190 cm^{-1} reflects the presence of a small amount of an enaminonitrile structure. The ^{1}H NMR spectrum (fig 5) shows that the heterocyclic structure is the major one. The relative proportion of heterocyclic/enaminonitrile structure is x/y = 79:21. The -CH_2-CN end group singlet at 3.5 ppm, allows the determination of cyanoacetamide group conversion (89%). $\overline{DP_n}$ is therefore close to 9, and $\overline{M_n} \approx 3\,000$ g mol^{-1} if macrocycle formation is neglected. The enaminonitrile structure was not detected in ^{13}C NMR spectrum.

• *Bulk polymerization*

At 160 °C in the presence of 1% *t*-BuOK, a rapid viscosity increase was observed after 15 min reaction. A poor compatibility between **3** and the catalyst can be noted. Both ^{1}H and ^{13}C NMR spectra (fig 6) show the presence of heterocyclic structure and a small amount of cyanoacetamide end groups. A small amount of enaminonitrile can also be detected (C^{10b}-C^{12b}). From ^{1}H NMR, the conversion is 82% and $\overline{M_n} \approx 1\,800$ g mol^{-1}. In the presence of 2% *t*-BuOK, stirring became impossible after 5 min reaction due to the very high viscosity. At that time, conversion was close to 97.5%, and $\overline{M_n} \approx 12\,000$ g mol^{-1}. The heterocyclic structure is still the main one, however the heterocyclic/enaminonitrile ratio decreases (x/y = 55:45). The same results were obtained using 2% SHDS as a catalyst instead of *t*-BuOK, while, as in the case of **1** dimerization, DBU led to a lower conversion. The polymerization results are summarized in table II.

The dimerization of *N*-alkylcyanoacetamides can be carried out in both solution, as previously shown by Schmitz and Schramm [1], and the bulk, in the presence of strong bases as catalysts. Polymers can be obtained by polymerization of compounds with two cyanoacetamido end groups. The application of this reaction to difunctional oligomers therefore seems to be promising for the synthesis of block copolymers.

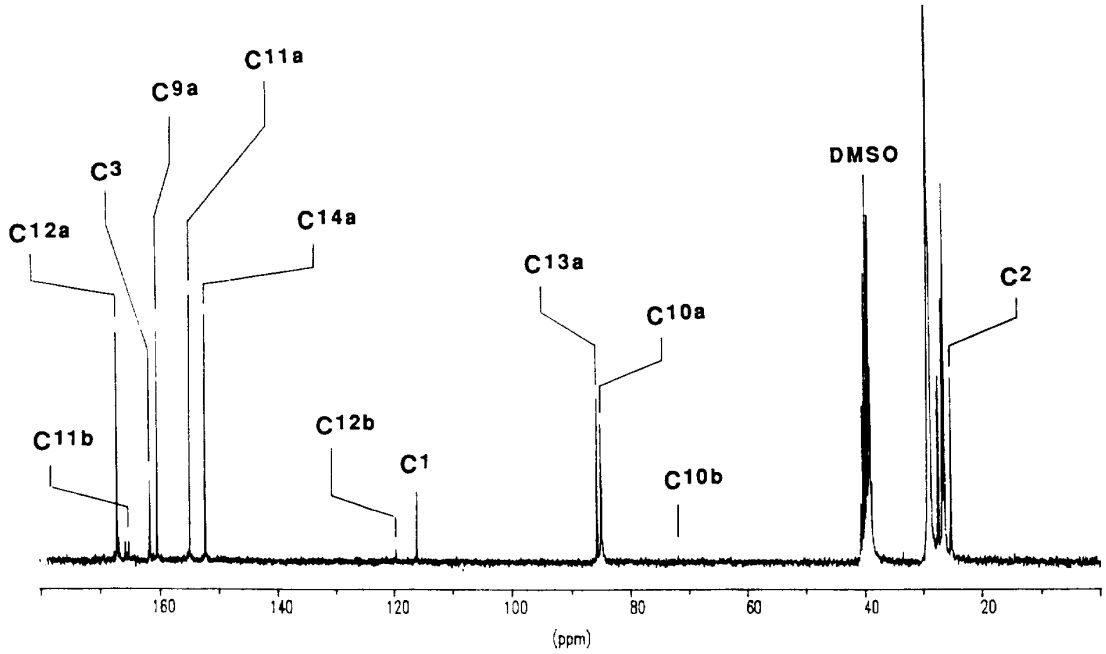


Fig 6. ^{13}C NMR spectrum (62.9 MHz, DMSO-d_6, ref TMS) of the polymer obtained by bulk polymerization of **3** (15 min, 160 °C, 1% *t*-BuOK). See figures 1, 4, 5 for numbering.

Table II. Solution and bulk polymerization of **3** in the presence of various catalysts (EtONa = sodium ethoxide, *t*-BuOK = potassium *t*-butoxide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Catalyst	Conversion	$\overline{M_n}$ (g mol^{-1})	Heterocycle/ enaminonitrile	T_g (°C)	$T_{5\%}$ (°C)
EtONa/EtOH, reflux	0.89$_0$	3 000	79:21	75	336
1% *t*-BuOK, 15 min, 160 °C	0.82$_0$	1 800	70:30	64	
2% *t*-BuOK, 1 h, 160 °C	0.97$_0$	12 000	55:45	119	354
2% DBU, 1 h, 160 °C	0.73$_0$	1 200	55:45	52	–

Fractional conversion, $\overline{M_n}$ and mol ratio heterocycle/enaminonitrile from ^1H NMR. Glass transition and 5% mass loss temperatures (T_g and $T_{5\%}$) from DSC and TGA.

Acknowledgment

Support for this investigation by DRET is gratefully acknowledged.

References

1 Schmitz E, Schramm S, *J Prakt Chem* (1982) 324 (1), 82

2 Baron H, Remfry FGP, Thorpe JF, *J Chem Soc* (1906) 85, 1726

3 Atkinson EFJ, Thorpe JF, *J Chem Soc* (1906) 89, 1906

4 Atkinson EFJ, Ingham H, Thorpe JF, *J Chem Soc* (1907) 91, 578

5 Schaefer JP, Bloomfield JJ, *Organic Reaction* (1967) 15, p 1-203

6 Taylor EC, Mc Killop A, *Chemistry of Enaminonitriles and o-Aminonitriles*, in *Advances in Organic Chemistry* (1970) 7, 1-415

7 Renner A, Moser R, Bellus M, Fuhrer H, Hosang O, Szekely G, *J Polym Sci, Part A: Polym Chem* (1988) 26 (5), 1361

8 Baldwin S, *J Org Chem* (1961) 26, 3288

9 Karle DW, *Ph D Thesis, University of Southern California, University Microfilms* (1965) 65

10 Krüger C, *J Organometal Chem* (1967) 9, 125