PREPARATION AND POLYMERIZATION OF 3-(2-ADAMANTYL)-3-METHYL-2-AZETIDINONE

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Dedicated to Dr M. Bohdanecký on the occasion of his 60th birthday.

3-(2-Adamantyl)-3-methyl-2-azetidinone (*VI*) was prepared, and new compounds, namely, methyl 2-(2-adamantyl) cyanoacetate, methyl-2-(2-adamantyl)-2-cyanopropanoate and methyl-2-(2-adamantyl)-2-methyl-3-aminopropanoate, were prepared in the course of the synthesis as intermediates. The anionic polymerization of lactam *VI* gave a polymer which was characterized by intrinsic viscosity, solubility, melting temperature and its IR and ^{1}H NMR spectra. Compared with 3-butyl-3-methyl-2-azetidinone, lactam *VI* polymerizes much more slowly.

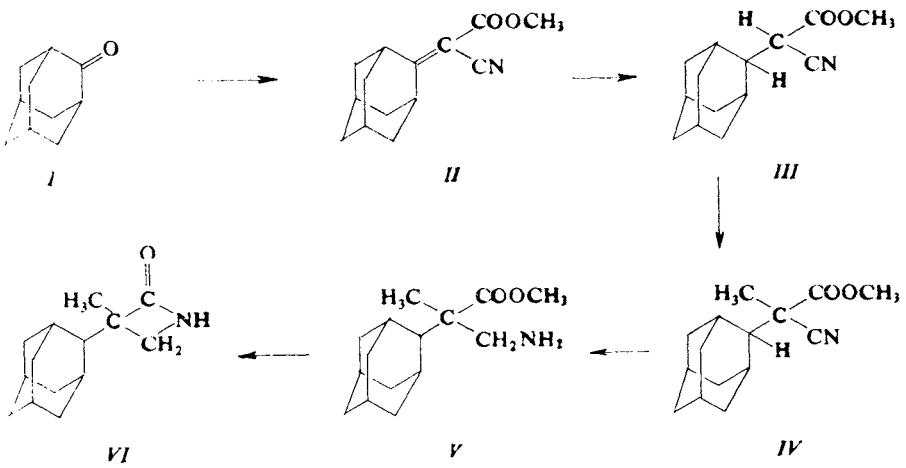
The effect of substitution on the polymerizability of lactams is best investigated by using 3,3-disubstituted four-membered lactams, as these polymerize anionically already at room temperature, without side reactions[1]. According to the reported data[2,3], the rate of anionic polymerization of 3-alkyl-3-methyl-2-azetidinones increases with increasing bulkiness of the substituent. This effect is explained by the increasing dissociation of the lactamate[2,3]. If such hypothesis were justified, then 3-(2-adamantyl)-3-methyl-2-azetidinone carrying the very bulky adamantyl residue should polymerize more quickly than, *e.g.*, 3-butyl-3-methyl-2-azetidinone. On the other hand, it may be expected that the growth reaction will be greatly impeded sterically due to the bulky substituent. The polymer of 3-(2-adamantyl)-3-methyl-2-azetidinone should possess a higher chain rigidity and poorer solubility than polymers of four-membered lactams substituted in position 3 with linear alkyl groups. These assumptions were checked by comparison polymerization of the respective lactams.

The procedure indicated in Scheme 1 was chosen for the synthesis of 3-(2-adamantyl)-3-methyl-2-azetidinone.

3-(2-Adamantyl)-3-methyl-2-azetidinone (*VI*) has in its IR and ^{1}H NMR spectra the basic characteristics of four-membered lactams and is comparatively poorly soluble, *e.g.*, in benzene and chlorobenzene.

The activated anionic polymerization of four-membered lactams proceeds even

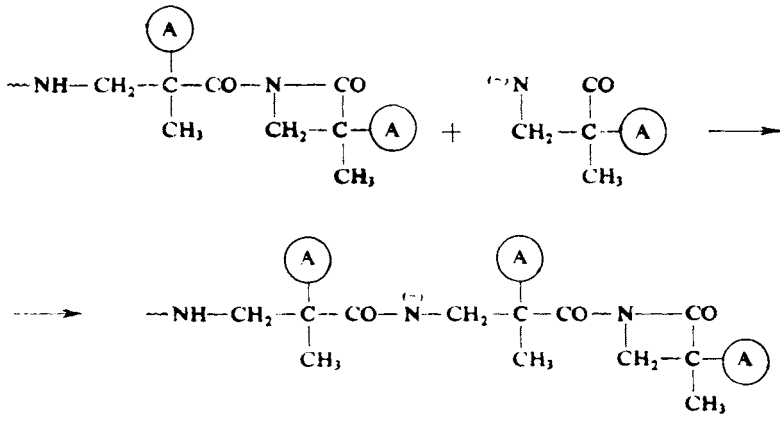
at room temperature at a rate which does not allow us to follow the polymerization by analyzing samples taken during its course. In contrast with the IR techniques used by other authors[2,3], the calorimetric method was chosen to compare the poly-



SCHEME 1

merization course[4]. In such experimental arrangement the measured temperature difference is directly proportional to the polymerization rate, because the heats of polymerization of lactams *VI* and 3-butyl-3-methyl-2-azetidinone (*VII*) are not essentially different. Preliminary experiments showed that at the same concentrations of the lactam, initiator and growth centres lactams *VI* and *VII* polymerize at such different rates that the ratio of polymerization rates cannot be estimated. Comparable rates can be achieved only by polymerizing lactam *VI* while using a ten times higher concentration of the growth centres (Fig. 1). As the rate of anionic polymerization of lactams is directly proportional to the concentration of the growth centres, it may be estimated that lactam *VI* polymerizes about twenty times more slowly than lactam *VII*. If, then, the hypothesis about the increase in the polymerization rate with increasing bulkiness of the substituent is valid at all[3], in the case of lactam *VI* the steric hindrance to the addition of the lactam anion to the growth centre, containing two bulky adamantyl moieties, is by far the prevailing effect. The calotte models of lactam *VI* and of the growth centre suggest that the reaction is sterically extremely demanding (Scheme 2).

The polymer of lactam *VI* has in its IR spectrum frequencies characteristic of the noncyclic amide group and of the cyclic carbonyl group of the N-acylated four-membered lactam, *i.e.* of the growth centre. The polymer possesses a comparatively low intrinsic viscosity and at room temperature is insoluble in acetone, benzene,



A = 2-adamantyl

SCHEME 2

chlorobenzene, nitrobenzene, 1,2-dimethoxyethane, acetonitrile, nitromethane, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1,2-dichlorobenzene, dimethyl sulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, formic and acetic acid. It is soluble in tetrahydrofuran to a limited extent only. The polymer dissolves well in N-methyl-6-hexanelactam, benzyl alcohol, hexamethylphosphortriamide, 1,2-dichloroethane, and chloroform. Thus, the polymer of lactam *VI* differs markedly in its solubility from that of lactam *VII* which dissolves in many more solvents, including benzene and 2-propanol.

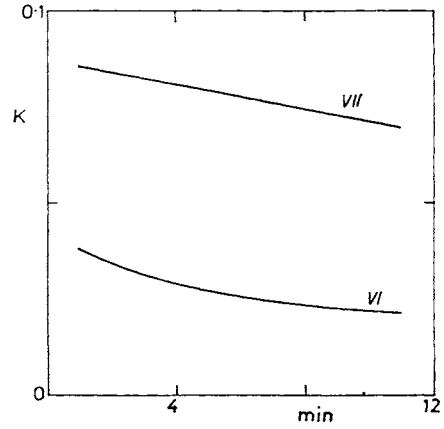


FIG. 1

The time dependence of temperature differences between the reaction cell and reference cell of the reactor in the polymerizations of lactams *VI* and *VII* in tetrahydrofuran (26·8°C). Initial concentrations of lactams *VI* and *VII* 0·104 mol/kg, of lithium lactamates 7 mmol/kg, of 1-pivaloyl-3-butyl-3-methyl-2-azetidinone 4·0 mmol/kg in the polymerization of *VI* and 0·3 mmol/kg in the polymerization of *VII* (lactams denoted at the respective curves).

EXPERIMENTAL

The melting points remain uncorrected. The infrared spectra were recorded with a Perkin–Elmer 457 apparatus in 2·5% solutions in tetrachloromethane, if not given otherwise. The proton NMR spectra were recorded with a JEOL-PS 100 apparatus in 0·5M solutions in tetrachloromethane, at 25°C, if not given otherwise. Chemical shifts are related to hexamethyldisiloxane as the internal standard (0·05 ppm).

Adamantanone was prepared according to ref.[5] Methyl 2-adamantylidenecyanoacetate (*II*) was prepared by the condensation of adamantanone with methyl cyanoacetate according to ref.[6]. IR spectrum: 1 730 (C=O) and 2 230 cm^{-1} (CN). ^1H NMR spectrum: 1·95 (m, 12 H, CH and CH_2 of adamantylidene), 3·20 (s, 1 H, 1′-H of adamantylidene), 4·20 (s, 1 H, 3-H of adamantylidene), 3·74 (s, 3 H, CH_3 of methoxyl). 3-Butyl-3-methyl-2-azetidinone (*VII*) and 1-pivaloyl-3-butyl-3-methyl-2-azetidinone were prepared according to ref.[7].

Methyl 2-(2-Adamantyl) Cyanoacetate (*III*)

A solution of 10·6 g of *II* in 140 ml methanol with 1 g of 10% Pd/C added was hydrogenated with intensive stirring at small overpressure (below 300 Pa). The theoretical amount of hydrogen was consumed within 5 h. The catalyst was removed by filtration, the remaining solution was evaporated, and the raw product was obtained in a quantitative yield. M.p. 41–43°C (hexane). IR spectrum: 1 752 (C=O) and 2 255 cm^{-1} (CN). ^1H NMR spectrum: 1·85 (m, 14 H, CH, and CH_2 of adamantyl), 2·25 (d, 1 H, J = 13 Hz, 2′-H of adamantyl), 3·67 (d, 1 H, J = 13 Hz, 2-H of ester), 3·73 (s, 3 H, CH_3 of methoxyl). For $C_{14}H_{19}NO_2$ (233·3) calculated: 72·07% C, 8·21% H, 6·00% N; found: 72·11% C, 8·16% H, 5·96% N,

Methyl-2-(2-adamantyl)-2-cyanopropanoate (*IV*)

Methylation of 5·55 g (23·8 mmol) ester *III* by employing a general procedure[7] gave 5·4 g (83·7%) of the raw product. M.p. 95·3–96·0°C (hexane). IR spectrum: 1 743 (C=O) and 2 245 cm^{-1} (CN). ^1H NMR spectrum: 1·55 (s, 3 H, 2-CH_3 of ester), 1·44–2·52 (m, 15 H, CH and CH_2 of adamantyl), 3·76 (s, 3 H, CH_3 of methoxyl). For $C_{15}H_{21}NO_2$ (247·3) calculated: 72·84% C, 8·56% H, 5·66% N; found: 72·61% C, 8·62% H, 5·61% N.

Methyl-2-(2-adamantyl)-2-methyl-3-aminopropanoate (*V*)

A mixture of 4·7 g (17·32 mmol) of ester *IV*, 7·5 g of the freshly prepared Raney nickel W2 and 0·8 ml of concentrated aqueous NH_4OH in 50 ml of methanol was hydrogenated in a 100 ml stainless steel autoclave at 100°C for 4 h and 12 MPa. After evaporaton of the filtrate, 4·5 g of a solid white compound was obtained, in the neutralization of which a theoretical amount of hydrochloric acid was consumed. After realkalization with a saturated aqueous Na_2CO_3 solution the released aminopropanoate *V* was extracted with ether, dried with Na_2SO_4 and finally purified by crystallization (2·52 g, 58%). M.p. 88–90°C (hexane). IR spectrum: 1 725 (C=O) and 3 415 cm^{-1} (NH_2). ^1H NMR spectrum: 1·21 (s, 3 H, 2-CH_3 of ester), 1·25 (1·09 at 62°C, both s, 2 H, NH_2), 1·73 (m, 17 H, CH, and CH_2 of adamantyl), 2·51 and 3·23 (AB-q, 2 H, J = 13 Hz, 3-CH_2 of ester), 3·62 (s, 3 H, CH_3 of methoxyl). For $C_{15}H_{25}NO_2$ (251·3) calculated: 71·67% C, 10·02% H, 5·5% N; found: 71·57% C, 9·98% H, 5·38% N.

3-(2-Adamantyl)-3-methyl-2-azetidinone (*VI*)

Cyclization of aminopropanoate *V* was performed using the Grignard reagent, by a slightly modified general procedure[8]. A solution of 2·31 g (9·19 mmol) of aminopropanoate *V* in 20 ml

of absolute tetrahydrofuran was added to 20 ml of ether solution of ethylmagnesium bromide (from 3·0 g ethyl bromide) while keeping temperatures and times according to the original paper. After decomposition with 10% HCl, the solvents were thoroughly removed by distillation, and the product was extracted with ether. The raw lactam, obtained in a quantitative yield, was purified by column chromatography (SiO_2, elution with benzene–ether), and after that, by repeated crystallization from benzene, acetone, and cyclohexane. M.p. 172—173°C. IR spectrum (KBr): 1 728 (C=O) and 3 200 cm^{-1} (NH); in absolute THF: 1 755 and 3 290 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): 1·31 (s, 3 H, 3-CH_3 of lactam), 1·74 (m, 15 H, CH and CH_2 of adamantyl), 2·84 and 3·25 (AB-q, 2 H, J = 4 Hz, 4-CH_2 of lactam), 6·38 (bs, 1 H, NH). For $C_{14}H_{21}NO$ (219·3) calculated: 76·67% C, 9·65% H, 6·39% N; found: 76·72% C, 9·67% H, 6·35% N.

Polymerization

Into the cell of a pseudoisothermal reactor[4], 20 ml in volume, 163·5 mg (0·746 mmol) of lactam *VI* was weighed, and dried 20 h at 100 Pa/20°C, after which it was dissolved in 8 ml of anhydrous tetrahydrofuran. After thermostating to 26·8°C, 44·4 µl of a hexane solution of butyllithium (1·189 mol/l) and 34·2 µl of a tetrahydrofuran solution of 1-pivaloyl-3-butyl-3-methyl-2-azetidinone (1·132 mol/l) were added. The polymerization course was followed by measuring the difference in temperatures between the polymerization and reference cell filled with 8 ml of tetrahydrofuran. In the homogeneous medium the polymerization proceeded only in the initial stage; after that, the polymer started to separate out. After 130 min, 0·45 ml of 0·13M acetic acid in tetrahydrofuran was added to the polymerization mixture. The reactor contents were rinsed with 50 ml of chloroform, and after evaporation of all solvents *in vacuo* the residue was dissolved in 40 ml of chloroform and extracted three times with 20 ml of water each time. Evaporation of the chloroform layer gave the polymer in a quantitative yield. IR spectrum (2·45% in $CHCl_3$): 1 630 (amide), 3 360 cm^{-1} (NH). ^1H NMR spectrum ($CDCl_3$): 1·36 (s, 3 H, CH_3). 1·76 (m, 15 H, adamantyl), 2·95 and 3·70 (2 × m, 2 H, CH_2), 7·90 (bs, 1 H, NH). $[\eta]$ = 0·0115 dl/g (chloroform, 25°C); m.p. (Kofler) 185—190°C.

Lactam *VII* was polymerized similarly, with the only difference that only 2·55 µmol of 1-pivaloyl-3-butyl-3-methyl-2-azetidinone in the form of a dilute solution was added. The results are summarized in Fig. 1.

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