polymer communications

Synthesis of *N*-acylated polyamides by the polymerization of *N*-acyl lactams

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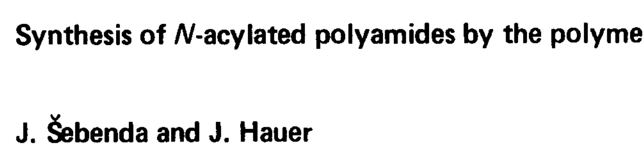
N-acylated polyamides described to date have been obtained by modification of non-acylated starting material. A typical scheme is the acylation of nylon-6,6 with acid anhydrides[1,2], and the subsequent exchange of acyl groups by means of acyl halides[3]:

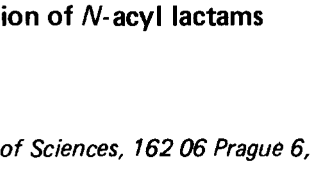


$$(-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-)_n + 2n(RCO)_2O \rightarrow (-CO-(CH_2)_4-CO-\underset{\underset{R}{|}}{\underset{CO}{\underset{|}{N}}}-(CH_2)_6-\underset{\underset{R}{|}}{\underset{CO}{\underset{|}{N}}}-)_n + 2n\,RCOOH \xrightarrow{(R'CO)_2O} (-CO-(CH_2)_4-CO-\underset{R'CO}{\underset{|}{N}}-(CH_2)_6-\underset{R'CO}{\underset{|}{N}}-)_n \quad (1)$$

However, fully acylated polyamides could also be obtained by polymerization of *N*-acylated lactams, assuming that this transformation is accompanied by a negative change in free energy and that an adequate reaction route is available.

It is known that substitution at the nitrogen atom considerably reduces the polymerizability of the lactam, so that *N*-substituted lactams may polymerize only if the lactam ring contains at least 8 ring atoms[4]. The 9-membered 8-octanolactam (capryllactam) is one of the most strained lactams. Its free energy of polymerization is –45.2 kJ/mol[5]. On thermodynamic grounds, the *N*-acylated capryllactams of the present study would be expected to polymerize the most readily of all the *N*-acyl lactams.

The polymerization of *N*-acyl lactams should proceed easiest with nucleophilic agents, similar to the anionic polymerization of lactams. When choosing polymerization initiators, one should bear in mind that *N*-acylated lactams undergo undesired side reactions. With strong alkalis they condense at room temperature, giving rise to *N*-acylated amides of 3-oxoacids[6]: for this reason, carboxylic acids were used as the initiators. If the initiating acid is derived from the exocyclic acyl of *N*-acyl lactam, the corresponding poly(*N*-acyl lactam) should arise as the only product of acidolysis:



(2)

We investigated the polymerization of *N*-acyl lactams Ia–Ic, both in bulk and in chlorobenzene solution. *Figure 1* shows the composition of the polymerization product at 57.6% conversion. In addition to the polymer and unreacted monomer (Ib), one can also see the individual oligomers (peaks 2–4), which prove step-growth polymerization.

Results listed in *Table 1* show that *N*-acyl lactams I polymerize acidolytically more quickly by several orders of magnitude than the unsubstituted lactam[7].

The ^{13}C n.m.r. spectrum of monomeric *N*-hexanoyl-8-octane lactam (Ic) exhibits two non-equivalent carbonyls

Table 1 Polymerization of *N*-capryl actams with carboxylic acids RCOOH

Monomer	mol/kg	Initiator R	Initiator mol/kg	Solvent	T (°C)	t (h)	Yield[a] (%)
Ia	4.00	C_6H_5	0.159	–	160	100	98.5[b]
Ib	1.34	$4\text{-}Cl\text{-}C_6H_4$	0.0402	C_6H_5Cl	160	90	96.7
Ib	1.34	$4\text{-}Cl\text{-}C_6H_4$	0.0402	C_6H_5Cl	180	24	98.6
Ic	4.12	$CH_3(CH_2)_4$	0.115	–	140	41	95.0

[a] Calculated from the monomer content determined by g.p.c.
[b] $[\eta]$ = 0.106 (in toluene at 25°C)

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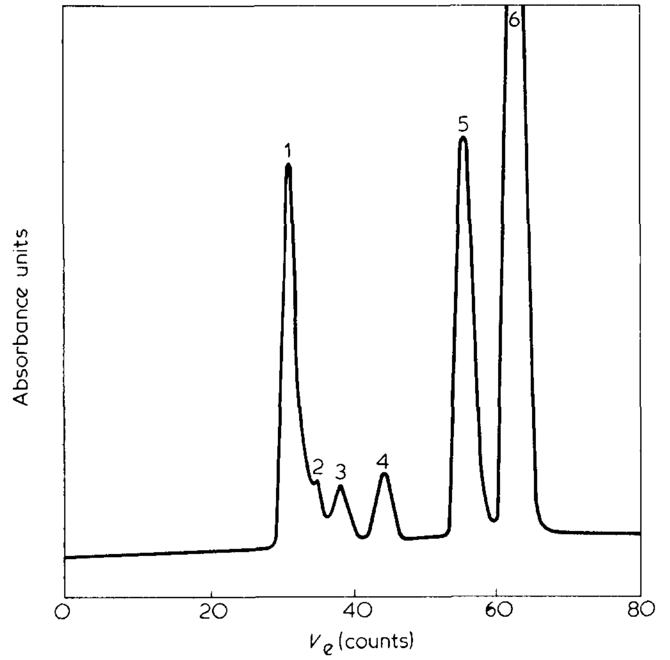
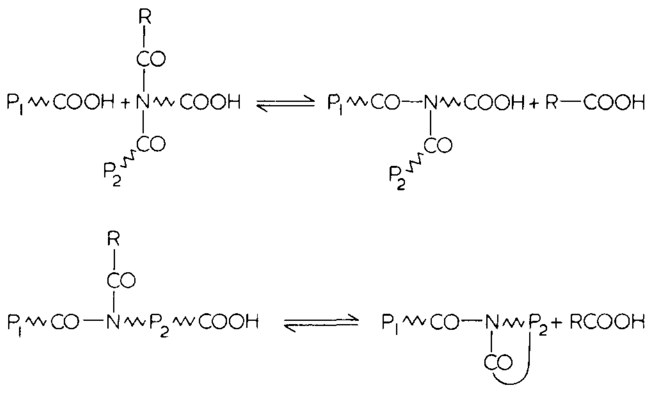


Figure 1 G.p.c. of the reaction product in the solution polymerization of Ib (1.43 mol/kg) initiated with 3 mol% of 4-chlorobenzoic acid in chlorobenzene (2 h/180°C): 1, polymer (M = 2000), 2, 3, 4, oligomers; 5, monomer Ib; 6, chlorobenzene

(chemical shifts 176.183 and 179.63 ppm), while the polymer exhibits only one type of carbonyl (δ = 176.183 ppm).

Aminolysis of 239 mg poly(*N*-benzoyl-8-octane lactam) with 94 mg of benzyl amine in 2.5 ml toluene at 50°C yielded turbidity already within 10 min; within 30 min, a large amount of precipitate was formed indicating deacylation of the polymer accompanied by formation of the unsubstituted polymer of 8-octane lactam. After 17 h of aminolysis/50°C, *N*-benzyl benzamide (m.p. 104°–106°C, ref 8 105°–105.5°C) was isolated from the filtrate.

The polymer of *N*-benzoyl-8-octane lactam (Ia) prepared with 4 mol % initiator possesses a comparatively low intrinsic viscosity (0.106 dl/g, Table 1), which may be due to the formation of branched polymers and macrocycles by inter- and intramolecular acidolysis.



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Infra-red emission studies of thin polymer films

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Polymers can be characterized by infra-red spectroscopy through the variation of their emittance, reflectance or transmittance with frequency. Transmittance is the method most commonly used to identify a material and reflectance is generally used to study the structure of polymers on surfaces[1,2]. Emittance is rarely utilized for the study of polymers because of the experimental difficulties involved[3]. For standard commercial instruments operating at room temperature, the radiation emitted or reflected from the spectrometer and sample holder can be much greater than the emission from a room temperature sample itself especially for thin polymer films.

This communication describes early results using a new method for obtaining emission spectra of thin polymer films with greatly enhanced sensitivity. Competing background radiation and spectral noise are greatly diminished by cooling the spectrometer and sample chamber. An experimental apparatus has been assembled which utilizes this reduced background advantage. It consists of a modified Digilab 296A Michelson interferometer with KBr beam-splitter at 77K, an ZnSe optical collection system also at 77K with the throughput matched to 4 cm^{-1} resolution, and a very sensitive Ge:Cu detector with shortpass cut-off filters operating at 4K. The polymer samples are spun onto freshly deposited metal substrates such as gold or aluminium. The samples are heat sunk to a copper block which is maintained between 80 and 500 ± 1K. Details of the experimental apparatus will be published later.

Typical observed emission spectra are shown in *Figure 1*. The sample was a 4000 ± 500 Å thick film of atactic polystyrene on an aluminium substrate. The film thickness was measured ellipsometrically. A freshly deposited gold sub-

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