Polymerization of Lactams: 57. G.l.c. and n.m.r. analysis of the anionic copolymers of 2-pyrrolidone with 6-caprolactam and 8-octanelactam

F. Chuchma, P. Trška, J. Roda and J. Králíček

Department of Polymers, Prague Institute of Chemical Technology, 166 28 Prague 6, Czechoslovakia

The activated anionic copolymerization of 2-pyrrolidone (PD) with 6-caprolactam (CL) or 8-octanelactam (OL) proceeds even above the ceiling temperature for PD homopolymerization. At high temperatures, the copolymerizations are accompanied by the depolymerization of PD sequences, which is more pronounced with the copolymers with CL. The copolymers obtained probably exhibit a constitutional heterogeneity and contain considerable amounts of low-molecular weight fractions. This may be the reason why the content of comonomers in the prepared copolymers determined by g.l.c. did not agree with that found by ^{1}H n.m.r. or ^{13}C n.m.r. spectroscopy. The copolymers with CL had in part a block structure and also an alternating character, depending on temperature and polymerization time, while random copolymers were obtained at high temperatures. The copolymers with OL tended mostly to alternation.

Keywords Activated anionic copolymerization; copolymers; 2-pyrrolidone and 6-caprolactam; 2-pyrrolidone and 8-octanelactam; gas liquid chromatographic analysis; spectroscopic analysis; ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy; sequence analysis

INTRODUCTION

At present, chromatographic techniques[1,2] (often in combination with mass spectroscopy), thermoanalytical[3-5] and spectral techniques are mostly employed in the analysis of copolyamides, and of the latter the most important is n.m.r. spectroscopy.

^{1}H n.m.r. spectroscopy has been used for the determination of comonomers in copolyamides prepared from both substituted and unsubstituted lactams[6]. For unsubstituted lactams the analysis is based on the determination of the number of $-CH_2-$ groups in a mean monomeric unit.

The ^{13}C n.m.r. spectroscopy provides, in addition to data on the quantitative representation of comonomers, fundamental information on the microstructure of copolyamides. Only the signal for the amide carbonyl is employed in the analysis, because its chemical shift is sensitive to neighbouring monomer units. Basic works in this field are the detailed studies of Kricheldorf[7-14] on the ^{13}C n.m.r. spectroscopy of homopolyamides derived from lactams[10,12] or diamines and dicarboxylic acids[10], strictly alternating copolyamides of both above mentioned types[9,11,13], and on random copolyamides[7,8].

The chemical shift of the $-CO-$ group in homo- and copolyamides is affected by the type of solvent, while the shifts are also influenced by the composition of the copolyamides[8,10,11].

Kricheldorf and coworkers also investigated a series of alternating copolymers of 2-pyrrolidone (PD) prepared

by condensation of a functionalized derivative of the equimolar compound 4-aminobutyric acid and another chosen ω-aminoacid. The alternating copolymers PD-glycine[9,13], PD-β-alanine[9], PD-6-caprolactam (CL)[9], PD-piperidone[9], some mixed aliphatic–aromatic copolyamides[14], and also terpolymers PD-β-alanine-glycine[11], PD-glycine-β-alanine[13], and CL-8-octanelactam (OL) -12-dodecanelactam[7] were preapred in this way.

Kricheldorf also performed the fundamental analyses of the ^{13}C n.m.r. spectra of the PD copolymers with CL or OL, which were prepared with the Na–benzoyl chloride initiation system[8]. The spectra of the homopolyamides and alternating copolyamides[9,10] were used to assign the signals in the obtained random copolyamide. It was found that the velocity of PD incorporation is lower than that for higher lactams (CL and OL) at 100°C.

The present work mostly concerns the ^{1}H and ^{13}C n.m.r. analyses of the copolymers of PD with CL or OL, prepared by activated anionic copolymerization at various polymerization temperatures.

EXPERIMENTAL

Purification and characteristics of 2-pyrrolidone[15], 6-caprolactam[16] and 8-octanelactam[17] were described earlier. The activator, N-benzoyl-2-pyrrolidone, was prepared according to ref. 15 (m.pt. 91°C); the polymerization initiator, potassium tert-butoxide, according to ref.

18. Copolymerizations were carried out in ampoules with two separated spaces for the solutions of the activator and initiator, respectively, in the mixture of monomers[19].

The gravimetric conversion was obtained after threefold extraction of polymers with methanol and the g.l.c. conversion, comprising also oligomeric fractions, by chromatographic analysis of the methanolic extracts.

The viscosity of the polymer solutions was measured according to ref. 15 and the intrinsic viscosity was calculated using the adapted[20] Loepelmann relationship[21]

$$[\eta] = 3.15(\sqrt[3]{\eta_{rel}} - 1)/c$$

The ¹H n.m.r. spectra were measured with a Varian XL100 spectrometer (100 MHz) at 90°C using hexamethyldisiloxane as an internal standard. The copolymers were dissolved in 100% formic acid (about 0.04 g/g HCOOH); their composition was calculated according to ref. 6. The mixtures for calibration of the ¹H n.m.r. spectra were prepared from homopolyamides of average viscometric degree of polymerization >200, prepared by nonactivated anionic polymerization[22].

The ¹³C n.m.r. spectra of the solutions of the copolymers in deuterated formic acid (about 0.15 g/g HCOOD) were measured with spectrometer Tesla BS567 (25 MHz) at 40°C under the following conditions: pulse length 10 μs (~35°C), interval between pulses 4 s, the gated decoupling of protons with suppressed Overhauser effect, standard HCOOD (166.3 ppm relative to tetramethylsilane).

RESULTS AND DISCUSSION

The copolymerizations of 2-pyrrolidone (PD) with 6-caprolactam (CL) or 8-octanelactam (OL) were carried out in the temperature region 55–150°C (see *Table 1*). Because it is known that the limiting temperature of the PD homopolymerization is about 80°C[23] and the homopolymerization of CL proceeds, to the contrary, only above this temperature[24] (the situation is similar with OL), the different reactivities of both comonomers and, consequently, the different composition of copolymers may be expected. PD is more reactive at lower temperature whereas CL (or OL) is more reactive at higher temperature, but PD is incorporated also above its ceiling temperature (this effect will be discussed in a subsequent paper[25]). The conversions determined by gas chromatography were always higher than the polymer content found gravimetrically, i.e. the polymerization mixture contains low-molecular weight portions soluble in methanol or in the methanol–lactams mixture (in detail see ref. 26). The analysis of extract by g.l.c. also enables to determine indirectly the representation of both comonomers in the copolyamide formed in this case by both the high-molecular weight polymer and the oligomers.

¹H n.m.r. spectroscopy gave substantially lower values of PD units in the copolymer than correspond to the nonpolymerized PD determined by g.l.c. of extracts. This discrepancy occurred even at high conversions of comonomers, where the g.l.c. and gravimetric data do not differ significantly, and thus cannot be ascribed only to the presence and various compositions of the oligomeric fractions. Therefore we investigated the ¹H n.m.r. spectra of model mixtures of homopolyamides, in which the

degree of polymerization $> 2.10^2$ made the effect of end-groups negligible. Surprisingly, the ratio of proton signals of internal $-CH_2-$, $-CH_2CO-$ and $-CH_2NH-$ methylenes did not correspond to the proportion of the polymeric mixtures, but always indicated a lower content of PD units. The deviation was more pronounced with the mixtures of PD and CL homopolymers. Assuming the same behaviour also with copolymers, we used the calibration relationship obtained by regression of homopolymer data also for copolymers. The following relationship was applied to copolymers of PD with CL:

$$X_{H_{CL}} = 7.43 \times 10^{-3} + 1.195 \times 10^{-2} Y - 2.033 \times 10^{-5} Y^2$$

where $X_{H_{CL}}$ is the corrected mole fraction of CL units and Y is the measured value of CL units in mol %. The equation is valid in the concentration interval of PD units 11–90 mol % with the standard deviation of $X_{H_{CL}}$ 1.49 $\times 10^{-2}$. The relationship for the mole fraction of OL in PD–OL copolymers was derived analogously:

$$X_{H_{OL}} = 2.593 \times 10^{-2} + 1.016 \times 10^{-2} Y - 2.920 \times 10^{-6} Y^2$$

This holds for the concentration interval for PD units of 11–89 mol % with the standard deviation of $X_{H_{OL}}$ 9.45 $\times 10^{-3}$.

Nevertheless, the content of PD in copolymers determined from the ¹H n.m.r. spectra, after the above correction on the real behaviour of homopolymer mixtures (X_H in *Table 1*), still differ from values obtained from g.l.c. analysis (X_G). This difference is more pronounced for lower yields of copolymers and could be explained in terms of the different compositions of extracted copolyamide and the low-molecular weight soluble fraction (but probably this does not hold for high conversions).

The observed discrepancies in copolymer analyses were overcome by ¹³C n.m.r. spectroscopy. To determine the copolymer composition, the region of response of the carbonyl carbon has been used, where signals corresponding to 4 sequences (dyads) of copolymerized monomers occur. The signals were assigned using the spectra of homopolymers, as described similarly by Kricheldorf[7-14].

According to published data, the chemical shift depends on the protonation power of the solvent, δ, being lower for HCOOD than for CF_3COOH, FSO_3H and D_2SO_4[8,10,12], which are stronger acids. A comparison of δ values for polymers of PD and CL are shown in *Table 2*. The average values of chemical shift corresponding to the signals of the homodyads and heterodyads of the copolyamides are given in *Table 3*.

The intensities of these signals were used for the determination of individual sequences in copolymers (C_i), mean lengths of homogeneous sequences (L), and the parameter χ, which expresses the deviation from the random character of the process (the system tends to alternation at $\chi > 1$ and to the block formation at $\chi < 1$). The results of the measurements are surveyed in *Table 1*.

¹³C n.m.r. spectroscopy mostly gave higher values of PD content in the copolymer than ¹H n.m.r. spectroscopy, the difference being clear-cut with the copolymers PD–CL. The ¹³C n.m.r. results did not coincide with the g.l.c. determinations in the case of PD–CL, but agreement was found for PD–OL within the limits of measurement errors (± 3 relative %), except for a few determinations.

Table 1 Anionic copolymerization of 2-pyrrolidone (PD) with 6-caprolactam (CL) and 8-octanelactam (OL) initiated by 1.5 mol% potassium tert-butoxide and 0.5 mol% N-benzoyl-2-pyrrolidone; the composition of copolymers determined by chromatography (X_G), ^1H n.m.r. (X_H) and ^{13}C n.m.r. (X_C) spectroscopy

B	X_S	T (°C)	τ (h)	$[\eta]$ (cm³/g)	(%)$_W$	(%)$_G$	X_G	X_H	X_C	C_{AA}	C_{AB}	C_{BB}	L_A	L_B	x
									(mol/mol)						
	0.67	150	19	83	46.6	56.3	0.431	0.381	0.397	0.108	0.480	0.412	1.45	2.72	1.00
	0.67	150	162	55	39.8	49.7	0.312	0.264	0.308	0.000	0.446	0.554	1.00	3.48	1.05
	0.67	115	18	95	41.4	49.2	0.548	0.475	0.482	0.163	0.616	0.221	1.53	1.72	1.23
	0.67	115	162	112	60.0	65.2	0.488	0.409	0.438	0.134	0.541	0.325	1.50	2.20	1.10
CL	0.50	80	18	83	27.5	35.9	0.568	0.450	0.499	0.153	0.691	0.156	1.44	1.45	1.38
	0.50	80	163	134	67.9	70.7	0.477	0.427	0.485	0.154	0.664	0.202	1.48	1.63	1.29
	0.67	55	8	35	8.6	23.8	0.838	0.890	0.913	0.905	0.095	0.000	20.05	1.00	0.60
	0.67	55	18	40	16.5	30.1	0.747	0.688	0.710	0.603	0.367	0.030	4.29	1.16	0.89
	0.67	55	162	80	41.0	41.7	0.723	0.669	0.643	0.466	0.497	0.037	2.88	1.15	1.14
	0.50	150	5	120	44.5	47.8	0.371	0.372	0.401	0.035	0.612	0.353	1.11	2.15	1.27
	0.50	150	163	84	70.2	74.9	0.268	0.215	0.276	0.000	0.619	0.381	1.00	4.25	0.95
	0.67	115	20	81	30.4	38.1	0.588	0.567	0.554	0.247	0.688	0.065	1.72	1.19	1.39
OL	0.67	115	69	121	53.3	62.5	0.545	0.526	0.504	0.142	0.729	0.129	1.39	1.35	1.46
	0.67	115	164	135	66.7	72.1	0.525	0.504	0.524	0.176	0.732	0.092	1.48	1.25	1.47
	0.33	80	15	57	11.1	13.8	0.565	0.555	0.527	0.133	0.832	0.035	1.32	1.08	1.67
	0.33	80	167	91	26.4	31.5	0.533	0.544	0.533	0.140	0.840	0.020	1.33	1.05	1.69

X_S — the content of PD in initial mixture (mol/mol); (%)$_W$ and (%)$_G$ — gravimetric and chromatographic conversions; T, τ — copolymerization temperature and time; $[\eta]$ — intrinsic viscosity; C_i — concentration of dyads in copolymer; L_i — mean length of homogeneous blocks in copolymer (A = PD, B = CL or OL); $x = C_{AB}/2 \cdot X_C(1 - X_C)$

Table 2 Effect of the solvent on δ (CO) of poly(2-pyrrolidone)
(PPD) and poly(6-caprolactam) (PCL)

Solvent	HCOOD	CF$_3$COOH	FSO$_3$H	D$_2$SO$_4$ (98%)
Polymer				
δ$_{PPD}$ (ppm)	177.04	178.56	179.06	179.91
δ$_{PCL}$ (ppm)	177.81	179.67	179.26	179.97

Table 3 Assignment of signals to homo- and heterodiads in the region of $\overset{|}{\underset{|}{C}}$=O response for copolymers of 2-pyrrolidone (PD) with 6-caprolactam (CL) or 8-octanelactam (OL)

B	PD–B	PD–PD	B–B	B–PD
CL	176.81	177.04	177.80	178.04
$\sigma_{CL} \times 10^2$	3	2	4	2
OL	176.79	177.08	178.06	178.35
$\sigma_{OL} \times 10^2$	2	2	2	2

However, the origin of this phenomenon is difficult to explain in terms of collected results.

The results shown in *Table 1* reveal highly significant differences in the reactivities of both comonomers which are dependent both on temperature and the polymerization time. The copolymers PD–CL, prepared at 55°C and with the initial molar ratio 2:1, contain prevailingly PD at short reaction periods. The CL units are incorporated into copolymer only as an alternating component. With the increasing polymerization time, the mean length of the homogeneous PD blocks gradually decreases and the character of copolymer changes from a block type to the random type.

Short homogeneous blocks of both lactams may be expected at 80°C and with initial equimolar amounts of comonomers. At this temperature, the reactivity of both comonomers is approximately equal and does not change significantly with reaction time. However, the relative reactivity shifts in the case of CL already at 115°C. In spite of the higher content of PD in the initial reaction mixture, the homogeneous PD blocks are shorter than CL blocks and this difference further increases with the extended polymerization time. The copolymer has a 'moderate' block character which disappears with the progress of polymerization time. Higher reactivity of CL is already clearly visible at 150°C. The average length of CL blocks grows with the increasing polymerization time and, to the contrary, the homogeneous blocks of PD completely disappear. The polymerization is accompanied by a decrease in polymer content (the content of low-molecular weight fractions increases: compare the polymer contents determined gravimetrically and by g.l.c.), with a substantial reduction in degree of polymerization and with the increase of free PD in polymerization product. The copolymer retains its random character.

Degradation reactions are clearly indicated at 150°C, and above all by the cleavage of PD–PD sequences and the base-catalyzed depolymerization by recyclization of PD. The detailed analysis of this phenomenon will be published in a subsequent paper[25]. Transamidation reactions between polymer chains catalysed by bases contribute to the random character of copolymers. It is also clear that the copolyamides based on PD and CL exhibit a constitutional heterogeneity, as it has been proposed by comparison of g.l.c. and ^{1}H n.m.r. analyses, and a variable microstructure reflected by changing diad concentration.

2-Pyrrolidone is more readily incorporated at the beginning of polymerization (cf. the changes of X_C, and also of X_H and X_G, with polymerization time and temperature), which is caused by a low rate of incorporation of the second lactam at low temperature, whereas the decrease of PD in copolymer at high temperature is due mainly to degradation (depolymerization) reactions.

Analogous character of copolymerization can be observed also with the pair of lactams PD–OL (see *Table 1*). However, the concentration of diads OL–OL is lower than of diads CL–CL in the PD–CL copolymers at the comparable polymerization conditions. This gives evidence of the lower polymerization activity of OL in the copolymerization with PD, in comparison with CL, for the given temperature interval. The copolymers have a considerable tendency to alternation, which increases with the extended polymerization time and decreasing copolymerization temperature. An interesting fact is that the mean length of homogeneous blocks is higher for PD (except at 150°C), as if the presence of OL (in comparison with CL) increases the ability of the PD to homopolymerize above its ceiling temperature.

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