Anionic copolymers of octanelactam with laurolactam (nylon-8/12 copolymers): 3. Glass transitions, heats of fusion, crystallinity and specific heats*

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Glass transition temperatures (T_gs), heats of fusion and crystallization and specific heats in the solid phase, for a series of statistical copolyamides (nylon-8/nylon-12), prepared by activated anionic polymerization of octane-/laurolactam (OL/LL), were determined and the results were correlated with the molar composition of the copolyamides and discussed. Minima for T_g and the heat of fusion for the initial melting and maxima for T_g/initial melting point (T_m) and changes in specific heat values were indicated for copolyamides with 50/50–60/40 molar compositions.

(Keywords: copolyamides; specific heat; glass transition; crystallinity; heat of fusion)

INTRODUCTION

The preparation and characterization of a new series of statistical copolyamides obtained by activated anionic polymerization of octanelactam (OL) with laurolactam (LL) (nylon-8/nylon-12) and some of their general properties have been previously reported[1]. In the second paper on this series of copolyamides [0/100–100/0 OL/LL (mol/mol)], the kinetic parameters of their isothermal crystallization were studied[2].

This paper describes a complementary study on the thermal properties, i.e. glass transition temperature (T_g), heats of fusion and crystallization, crystallinity and specific heats in the solid phase for the same copolyamides. The results were correlated with the molar composition of the copolyamides and with literature data for the corresponding homopolymers nylon-8[3–7], nylon-12[5,8–11] and the relevant copolyamide series[9,10,12] and discussed. The individual copolymers have been denoted, as previously, by their molar ratio composition in OL and LL.

EXPERIMENTAL

Materials

The copolyamide samples of OL and LL used are the same as those described in a previous paper[1].

Glass transition temperatures

A Mettler DSC-30 connected with an IBM PC 2/60 and an Epson (X-60) printer were used to record all the measurements. In order to maximize the amorphous content, the samples were heated to 20°C above the return temperature of the melting curve to the baseline[13] and cooled rapidly at 320°C min^{-1} to -100°C under N_2 atmosphere. The heating rate for the T_g determination (mean transition temperature) was 10°C min^{-1}, and at least two scans, starting from -25°C, were run for each copolyamide.

Heats of fusion and crystallization

A Perkin-Elmer differential scanning calorimeter (DSC-2) operating at heating/cooling rates of 10°C min^{-1} and calibrated against pure indium was used. The melting exotherm was recorded for each specimen under N_2 atmosphere to 20°C above the return temperature of the exotherm to the baseline, and then the specimen was cooled to 45°C, equilibrated, and reheated to obtain the crystallization and remelting curve. Heats of fusion for the initial melting (ΔH_m) and remelting ($\Delta H'_m$) and heats of crystallization (ΔH_c) were obtained from the areas of the appropriate peaks measured by planimeter at least five times.

Specific heats

The specific heats (C_p values) were determined by a Perkin-Elmer DSC-2 in the range of 50–90°C, according to the manufacturer's instructions[13], using the following formula:

$$C_{P_{\text{sample}}} = \frac{W_{\text{sapphire}}}{D_{\text{sapphire}}} \times \frac{D_{\text{sample}}}{W_{\text{sample}}} \times C_{P_{\text{sapphire}}}$$

where W is weight (mg) and D is the displacement of the ordinate axis from the baseline (cm). The specific heats of the sapphire reference sample at 50°C and 90°C were 0.79789 and 0.93312 J g^{-1} K^{-1}, respectively[13]. Since the differences in the weight between the pans of the reference

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and the samples were negligible (<0.1 mg), no correction to the displacement (D_{sample}) was necessary.

RESULTS AND DISCUSSION

The T_g values for two samples of each copolyamide were found to be either the same or very similar. The average values for all the OL/LL copolyamides are given in *Table 1*.

The higher T_g of nylon-8 than that of nylon-12 of a higher molecular weight[1] (*Table 1*), is attributed to the higher amide group density of the former. This forms a denser hydrogen bond network[8] and more dipole–dipole interactions through the partial amide double bond[14], resulting in a higher rotation barrier (inflexibility in T_g). The T_g value for nylon-12 (*Table 1*) is in agreement with those previously found, 42°C[8] and 37°C[9] (same range of $\bar{M}_n$) for the anionically and hydrolytically prepared samples, respectively. The same applies for the value of nylon-8 compared to that in a previous paper of 50°C[3] (same range of $\bar{M}_n$). However, a significantly lower T_g (30°C) for the hydrolytically prepared nylon-8, having a similar molecular weight to that in this study[1], was reported[4]. This value is similar to that of nylon-12 and contradicts the above dependence of T_g on the density of amide groups in the homopolyamides. Hence, this should be due to the different conditions of preparation affecting the T_g of the product, since the cooling conditions of the sample melts (cold crystallization) were, in both cases, similar and no significant dependence of T_g values on the cooling conditions of the melts was observed for nylon-12 and nylon-6[9].

T_g values *versus* molar composition of the OL/LL copolyamides (*Table 1*) showed a progressive decrease from the homopolymers to a minimum for the 50/50 (OL/LL) copolyamide, as in the case of the melting points[1]. A T_g minimum was also observed for the anionic statistical copolyamides of capro-/laurolactam (CL/LL) at the same molar composition (50/50 CL/LL) and the reported interpretation of this minimum[10] also applies to the present paper. The depression of T_gs from the value of nylon-12 to that of the minimum, was smaller for the OL/LL copolyamides (8.3°C) than for CL/LL (22°C)[10], on account of the greater molecular and crystalline similarities of the components in the former (nylon-8/12) than in the latter (nylon-6/12)[1]. It is obvious that the Gordon–Taylor[15] equations and the simplest Fox[16] equation are not applied to the present series of copolyamides, since the relationship of T_g *versus* weight fraction of the components is not linear, but with a minimum, as in the case of CL/LL copolyamides[10].

The values of the T_g/T_m ratio (where T_m is the initial melting point) for the OL/LL copolyamides (*Table 1*), are in good agreement with the average empirical value (~ 0.66) for most polymers[7]. These values *versus* the copolyamide composition produced a curve with a maximum for the 60/40 (OL/LL) composition, as in the case of CL/LL copolyamides[10]. Similar values of the T_g/T_m ratio were also obtained applying the remelting points[1], instead of the initial melting points.

It is known that the T_g is due to the amorphous phase of the polymers and obviously the percentage weight composition of the amorphous phase of the present semicrystalline copolyamides must have a different chemical composition in OL/LL from that of the whole copolyamides[1]. By using the crystallinity values found from the density[1] or from the heat of melting (*Table 2*) and the results of the X-ray diffraction patterns[1] for the OL/LL copolyamides [the crystalline character of the LL- and OL-rich copolyamides is entirely polylaurolactam (PLL) and polyoctanelactam (POL) type, respectively], the percentage weight of OL content in the amorphous phase for each copolyamide was calculated[10]. Plotting these values against the weight composition of the whole copolyamides (*Figure 1*) showed that the OL/LL copolyamides fall into two separate groups (0/100-50/50-100/0 OL/LL) determined by the prevailing crystalline entities present, as in the case of CL/LL copolyamides[10].

The participation of the 50/50 OL/LL copolyamide in both groups, in this paper, is in agreement with the X-ray patterns[1]. The same classification of this series of copolyamides for the two groups was also derived from isothermal crystallization data, correlating the half-time crystallization to the crystallization temperature[2]. In addition, plots of Flory's equation parameters, correlating the reciprocal of the thermodynamic melting point ($10^3/T_m^\circ$) to the logarithmic molecular fraction ($-\ln N_A$) of the major component (OL or LL) of the copolyamides, afforded the same classification (*Figure 2*) by using the approximate initial melting point of the sample[1] as T_m°. An analogous result was also reported for the statistical nylon-6/12[10] and nylon-6/66[12] copolyamides.

Heats of fusion, crystallization and crystallinity

The heats of fusion and crystallization were found by d.s.c. for at least three samples of each copolyamide. Their averages and their extreme values are given in *Table 2*.

The heat of fusion found for nylon-12 in this study ($56.48\,\mathrm{J\,g^{-1}}$) was in agreement with previously published values for anionic nylon-12 [56.07 (ref. 5), 69.45 (ref. 9), 58.16 (ref. 10) and $53.56\,\mathrm{J\,g^{-1}}$ (ref. 11)]. However, the value of $48.53\,\mathrm{J\,g^{-1}}$ for nylon-8, which approximates to $40.59 \pm 1.68\,\mathrm{J\,g^{-1}}$ for the hydrolytically prepared sample[4], is much lower than that ($74.89\,\mathrm{J\,g^{-1}}$)[5] for the anionic sample, whereas a great range of values (29.29–$104.60\,\mathrm{J\,g^{-1}}$) was reported for nylon-8 under various conditions[6].

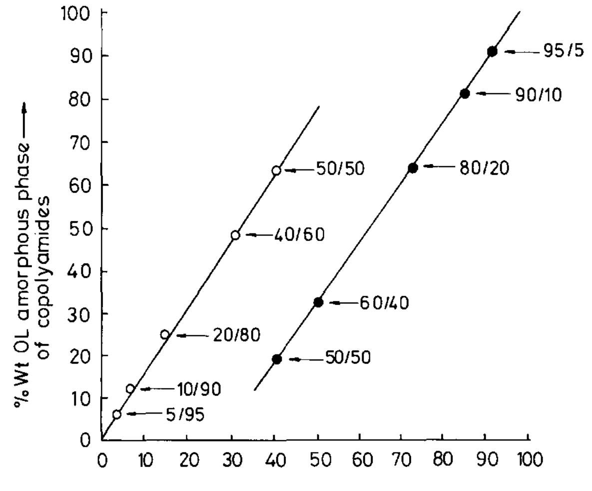

Figure 1 Weight percentage of OL units in the amorphous phase *versus* weight percentage in the whole OL/LL copolyamide

Table 2 shows a sharp fall in the heats of fusion, crystallization and remelting with copolymerization to a minimum for the 60/40 (OL/LL) copolyamide, as for the (re)melting points[1]. An analogous minimum of the above heats for the 50/50 molar composition was observed for nylon-6/12 copolyamides[10]. The observed substantial difference between ΔH_m and $\Delta H'_m$ values (*Table 2*) for the intermediate composition copolymer (40/60-60/40 OL/LL) is due to their slow crystallization rates under the d.s.c. measurement conditions.

The crystallinities of the copolyamide samples were calculated from the ΔH_m and $\Delta H'_m$ values (*Table 2*), by the use of the relationship:

$$K = \Delta H_m / \Delta H_u$$

where ΔH_u is the heat of fusion of the crystalline phase of each copolyamide (nylon-12 for the 0/100-50/50 OL/LL or nylon-8 for the 60/40-100/0 OL/LL copolyamides). The ΔH_u values for nylon-12 and nylon-8 were calculated as 224.68 and 207.53 J g^{-1}, respectively, from the contribution of their structural groups (3765.6 J mol^{-1} –CH$_2$–, 2928.8 J mol^{-1} –CONH–)[7]. These values were applied to the 0/100-50/50 OL/LL and 60/40-100/0 OL/LL copolyamides, respectively, assuming that incorporation of the minor comonomer units into the PLL or POL crystals does not substantially change their heat of fusion. The crystallinities for both initial and recrystallized samples (*Table 2*) showed a minimum for the 60/40 OL/LL copolyamide, which corresponds approximately to equal weights of OL (51.77%) and LL units. A similar result was also reported for nylon-6/12 copolyamides[10].

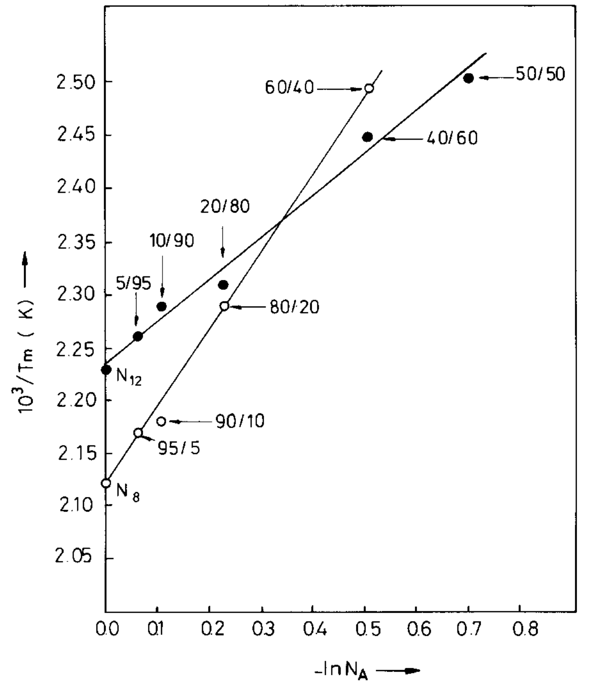

Figure 2 Relationships between Flory's equation parameters for the OL/LL copolyamides

The crystallinity values calculated from the densities[1] were considerably higher than those from the heats of fusion (*Table 2*), but both methods showed the minimum crystallinity to appear at the same composition (60/40 OL/LL). These differences, besides the deviations due to determinations of crystallinity by different methods, should be attributed to the use of theoretical values for ΔH_u, instead of experimental values, which are not available in the literature.

Specific heats

Specific heat values obtained from d.s.c. measurements of three samples for each copolyamide showed small differences (0–0.084 J g^{-1} K^{-1}). Their values at 50 and 90°C (*Table 3*) show an increase with the extent of copolymerization, with a maximum within the range 40/60-50/50 OL/LL. A similar C_p maximum within the same composition range was also observed in the case of CL/LL copolyamides[9]. The observed increase in C_p against the copolymerization extent was attributed to the corresponding crystallinity decrease of the copolyamides (*Table 2*). This suggestion is confirmed by the fact that polymers with the same composition show higher C_p values for lower crystallinity and density[17]. A higher C_p value for nylon-12 than for nylon-8, despite the higher crystallinity of the former, was observed, as for nylon-12 and nylon-6[9].

Table 1 Characterization data of the OL/LL (co)polyamides

Polyamide OL/LL (mol/mol)	DSC-2 (°C) $T_m{}^a$	$T_c{}^b$	$T'_m{}^c$	T_g	T_g/T_m	$\bar{M}_n{}^d$	$[\eta]^e$ (dl g^{-1})	d^f (g cm^{-3})
0/100 (Nylon-12)	176.0	145.8	175.5	42.0	0.70	27 100	1.80	1.010
5/95	169.0	131.3	170.7	40.5	0.71	26 320	1.72	1.011
10/90	164.3	129.0	164.7	39.0	0.71	25 710	1.71	1.012
20/80	160.0	121.0	160.0	36.5	0.71	25 020	1.56	1.014
40/60	136.6	95.0	138.7	34.0	0.75	24 210	1.42	1.020
50/50	127.0	–	126.0	33.7	0.77	23 510	1.32	1.023
60/40	128.3	95.0	119.5	35.0	0.77	22 810	1.16	1.028
80/20	165.0	119.6	165.0	41.0	0.72	21 080	1.00	1.040
90/10	186.1	146.5	187.0	45.8	0.69	19 890	0.87	1.047
95/5	188.0	150.3	188.3	46.7	0.69	19 600	0.80	1.050
100/0 (Nylon-8)	197.0	160.0	197.6	51.1	0.69	19 250	0.71	1.056

[a] Melting temperature of the initial sample (maximum peak of first run)

[b] Crystallization temperature by cooling from 20°C above T_b (temperature of the return to baseline after T_m)

[c] Remelting temperature after equilibrating at 40°C and reheating

[d] Measurements with membrane osmometer (Knauer)[1]

[e] Intrinsic viscosity using *m*-cresol at 25°C[1]

[f] Mean value of densities determined both pycnometrically with toluene and by means of a carbon tetrachloride/ethanol density gradient column[1]

Table 2 Heats of melting (ΔH_m first cycle, $\Delta H'_m$ remelting) and crystallization (ΔH_c) and percentage of crystallinity calculated from the heat of melting

Polyamide OL/LL (mol/mol)	ΔH_m(J g^{-1})	ΔH_c(J g^{-1})	$\Delta H'_m$(J g^{-1})	% Crystallinity	
				Initial samples	Recrystallized samples
0/100 (Nylon-12)	56.48 (55.23–58.16)	47.28 (41.84–51.88)	56.90 (53.97–59.41)	25.2	25.4
5/95	53.14 (51.46–56.48)	39.33 (38.07–41.42)	47.70 (40.58–53.97)	23.7	21.2
10/90	45.61 (37.66–50.21)	39.33 36.40–41.42)	42.68 (34.73–49.79)	20.2	18.9
20/80	38.49 (33.47–42.26)	30.54 (28.45–32.64)	35.15 (29.71–42.26)	17.2	15.7
40/60	32.22 (29.29–33.89)	19.25 (13.39–25.52)	17.99 (16.32–20.08)	14.4	7.9
50/50	28.45 (27.61–29.71)	–^{a}	17.99 (15.90–20.08)	12.7	8.0
60/40	11.72 (11.30–11.72)	9.21 (8.79–9.62)	11.30 (10.04–12.13)	5.6	5.4
80/20	28.45 (24.69–32.22)	26.78 (24.69–30.54)	27.61 (24.69–30.54)	13.7	13.3
90/10	43.93 (41.42–49.37)	35.56 (33.47–37.24)	41.00 (38.49–43.93)	21.3	19.7
95/5	43.51 (38.49–51.05)	39.33 (38.07–41.42)	49.37 (45.19–51.46)	20.9	23.7
100/0 (Nylon-8)	48.53 (44.35–53.14)	41.84 (38.49–44.35)	49.37 (43.51–55.65)	23.5	23.8

^{a} No crystallization curve observed in the conditions of scanning

Table 3 Specific heat (C_p) of the OL/LL (co)polyamides at 50 and 90°C

Polyamide OL/LL (mol/mol)	C_p(J g^{-1} K^{-1})	
	50°C	90°C
0/100	1.30	1.46
5/95	1.30	1.59
10/90	1.34	1.67
20/80	1.42	1.76
40/60	1.51	1.97
50/50	1.51	1.97
60/40	1.38	1.59
80/20	1.21	1.46
90/10	0.96	1.21
95/5	0.88	1.13
100/0	0.79	1.00

The C_p value for nylon-12 in this paper (1.30 J g^{-1} K^{-1}) is significantly higher than that in the literature (0.71 J g^{-1} K^{-1}). This led to the calculation of the theoretical C_p value for nylon-12 according to the group contributions[7], which gave a value of 1.97 J g^{-1} K^{-1}, considerably closer to that found in this paper than to the referred value. Finally, no C_p values for nylon-8 could be found in the literature in order to compare them with the values found in this paper.

REFERENCES

1 Kehayoglou, A. H. and Arvanitoyannis, I. *Eur. Polym. J.* 1990, **26**, 261
2 Arvanitoyannis, I. and Keyayoglou, A. H. *Angew. Makromol. Chem.* in press
3 Champetier, G. and Pied, J. P. *Makromol. Chem.* 1961, **44**, 64
4 Ceccoruli, G., Manescalchi, F. and Pizzoli, M. *Makromol. Chem.* 1975, **176**, 1163
5 Kubota, H. and Howell, J. B. *J. Appl. Polym. Sci.* 1975, **19**, 1521
6 Illers, L. H. and Haberkorn, H. *Makromol. Chem.* 1971, **146**, 267
7 Krevelen, D. V. 'Properties of Polymers', Elsevier, Amsterdam, 1972, pp. 70, 74, 78, 130, 390
8 Gordon, G. *J. Polym. Sci. A2* 1971, **9**, 1963
9 Godovskii, U. K., Duvonik, I. I., Ivanova, S. L., Kurashev, V. V., Frunze, T. M. and Slonimskii, G. L. *Polym. Sci. USSR (Eng.)* 1977, **19**, 453; *Vysokomol. Soyed.* 1977, **A19**, 392
10 Goodman, I. and Kehayoglou, A. H. *Eur. Polym. J.* 1983, **19**, 321
11 Goodman, I. and Valavanidis, A. *Eur. Polym. J.* 1984, **20**, 241
12 Harvey, E. D. and Hybart, F. *J. Appl. Polym. Sci.* 1970, **14**, 2133
13 Perkin-Elmer Manual, Differential Scanning Calorimeter DSC-2, New York, 1974
14 Botta, A., Cancia, F. and Palumbo, R. *J. Appl. Sci.* 1985, **30**, 1669
15 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2**, 493; Brydson, J. A. in 'Polymer Science' (Ed. A. D. Jenkins', Vol. 1, North-Holland, Amsterdam, 1972, p. 210
16 Fox, T. *Bull. Am. Phys. Soc.* 1956, **1**, 123
17 Wilski, H. in 'Polymer Handbook' (Eds J. Brandrup and I. H. Immergut), 2nd Edn, John Wiley & Sons, London, 1975, pp. 111–215