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On the First-Order Transitions of Hydrogen-Bonded Liquid-Crystalline Poly(ester amides)

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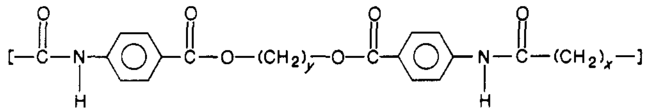
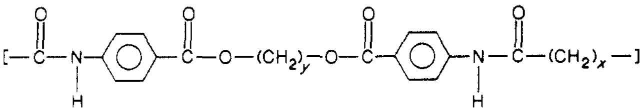
ABSTRACT: The heats and entropies of 46 strictly alternating, hydrogen-bonded highly regular poly(ester amides) were obtained from the reproducible first-order endotherms in their DSC heating scans. The total heats of transition, ΔH°_{tot}, are in good agreement with literature values and group additivity calculations. All poly(ester amides) with $y = 2$, most of those with $y = 4$, and several with either very small x or $x = 20$ melt in a single step. The other ones, especially those with $8 \leqslant x \leqslant 14$ and $y = 3$ or $y = 5$, change from the crystalline to the isotropic state in several stages. The existence of three to four mesomorphic phases among the latter polymers is demonstrated by the number of transitions and the sizes of the heats of transition, as well as by hot-stage cross-polarized light microscopy. X-ray studies in a previous work[1] indicated at least one of the mesomorphic phases to be a smectic C or a twisted smectic C phase. Poly(ester amides) with $y = 3$ or $y = 5$ and $1 \leqslant x \leqslant 8$, as well as those with $y = 9$, exhibit two or three endotherms. Each of these endotherms is significantly smaller than ΔH°_{tot} or ΔH°_m, the expected heat of melting, yet their sum is in good agreement with ΔH°_{tot}. These polymers exhibit, hence, one or two mesomorphic phases. The specific nature of these phases for individual polymers is not known at present but microscopy observations lead us to believe that the first mesomorphic phase above the crystal/liquid crystal transition is a high-viscosity smectic phase. This phase converts to the isotropic melt when $x \leqslant 8$, or to a far lower viscosity smectic phase when $y = 3$ and $y = 5$ and $8 \leqslant x \leqslant 14$. At even higher temperature, the low-viscosity mesomorphic phase converts in one or two steps to an isotropic melt.



Introduction

In a recent publication[1] the preparation and characteristics of a new family of hydrogen-bonded liquid-crystalline poly(ester amides) were described. Here x stands for the number of methylene groups between the amide residues and y is the number of methylene groups between the ester moieties. These poly(ester amides) will be denoted by their y and x values throughout this paper. The unique structural features of these polymers are their high regularity and strict alternation of two amide groups and two ester groups, the substitution of each aromatic ring in the para position by one amide and one ester group, and the fact that these reactive groups are pairwise connected by alkylene chains. The alkylene chains contain between one and 20 methylene groups. All amide residues are intermolecularly interacted with each other by hydrogen bonds (H-bonds) between adjacent chains. The H-bonds appear to exist over a broad temperature range, traversing the crystalline as well as the mesomorphic intervals.



Thermotropic liquid crystallinity was demonstrated in ref 1 by (a) the presence of multiple reproducible endotherms in the heating cycle of differential scanning calorimetry (DSC) scans, (b) the coexistence of sample mobility or spontaneous fluidity together with birefringence during observations in a hot-stage cross-polarized light microscope, and (c) the wide-angle X-ray diffraction (WAXD) patterns obtained from the crystalline polymers, their birefringent states, and isotropic melts, as well as from quick-quenched oriented and unoriented samples. The flat-plate X-ray patterns of oriented poly(ester amides) with $7 \leqslant x \leqslant 14$ were characterized by paucity of reflections and the complete absence of nonequatorial and nonmeridional reflections. Figure 1, for $y = 3$ and $x = 14$, is characteristic.

In this paper a study of some thermodynamic aspects of the first-order transitions of the poly(ester amides) will be presented. Experimentally, the investigation was conducted by DSC scans and cross-polarized light microscopy. In both procedures the heating and cooling rates were maintained at 10 K/min unless specified otherwise. The first-order transition points were all determined from the positions of the corresponding peaks in DSC scans[2,3] conducted at 10 K/min. The results of up to eight scans per polymer were averaged to obtain the reported temperature and heat of each transition. Throughout this paper all heats of transition, ΔH, are in units of kilojoule per mole. Crystallinity indices were obtained by conventional methods from WAXD powder diagrams. Details of the experimental procedures were published in ref 1.

Results and Discussion

DSC and cross-polarized light microscopy studies of the poly(ester amides) were presented in paper 1.[1] The per-

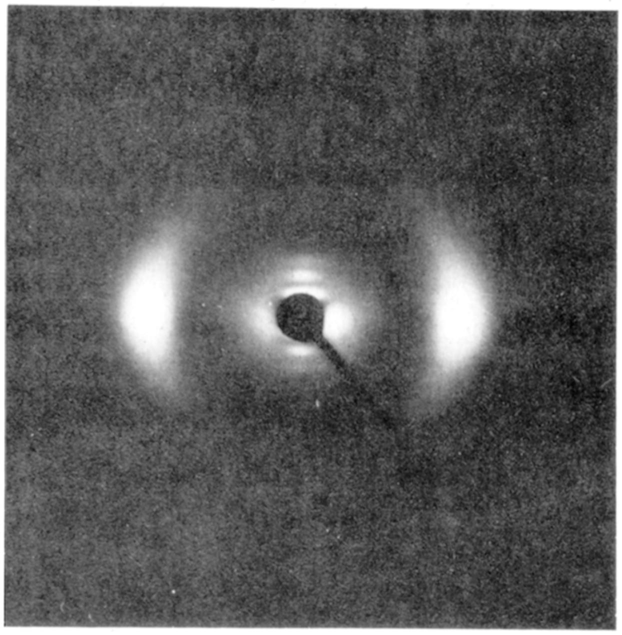


Figure 1. X-ray fiber diagram of the poly(ester amide) $y = 3$, $x = 14$. The unsymmetrical inner equatorial reflection is a beamstop artifact and should be disregarded.

tinent observations are summarized below. The presence upon heating of a single reproducible endotherm in the DSC scans of all poly(ester amides) with $y = 2$, combined with microscopy observations, indicates the endotherm to be a simple melting point, T_m. This is supported by a single crystallization exotherm appearing at substantial supercooling during cooling in the DSC instrument. The situation is dramatically different in the case of poly(ester amides) with $y = 3$, 5, and 9 and several of those with $y = 4$. All members of these families, except for those with $y = 4$ and $x = 2n$, showed two or more reproducible first-order transitions upon heating from ambient temperature to the isotropic melt. In instances where $x \geqslant 8$ and $y = 3$ or $y = 5$, there appeared several minor reproducible transitions at temperatures above the uppermost major endotherm in the heating cycles of the DSC scans. The minor transitions became more pronounced with increased x up to $x = 14$ and are clearly associated with mesomorphic behavior.

In all instances where high-temperature minor transitions were observed during the heat cycle of DSC scans, intense birefringence of the mobile poly(ester amides) became very noticeable, usually at the uppermost major endotherm or above it upon approaching the first higher minor exotherm. This birefringence appeared grainy and devoid of unique structural features. In the temperature interval between the minor transitions, the birefringence was substantially duller than at lower temperatures. It finally faded away above the uppermost minor transition. Figure 2, for $y = 3$ and $x = 10$, is typical. It follows the polymer from the solid state (panel A) through the intense birefringence interval (panels B and C) to the dull birefringence zone (panel D). A spontaneous flow of the birefringent poly(ester amides) was observed in all cases where $y = 3$ and $x + y = 2n + 1$ (odd) and for the special case of $y = 3$ and $x = 3$ where $x + y = 2n$ (even). In the $y = 4$ family, intense birefringence coupled with spontaneous flow appeared for the members with $x = 5$, 7, and 11 but not for $x = 3$. The $y = 5$ family followed the $y = 3$ family: all polymers with $x + y = 2n + 1$ and $x = 11$ showed intense birefringence with spontaneous flow while the even members (except for $x = 11$) developed intense birefringence upon softening but no spontaneous flow.

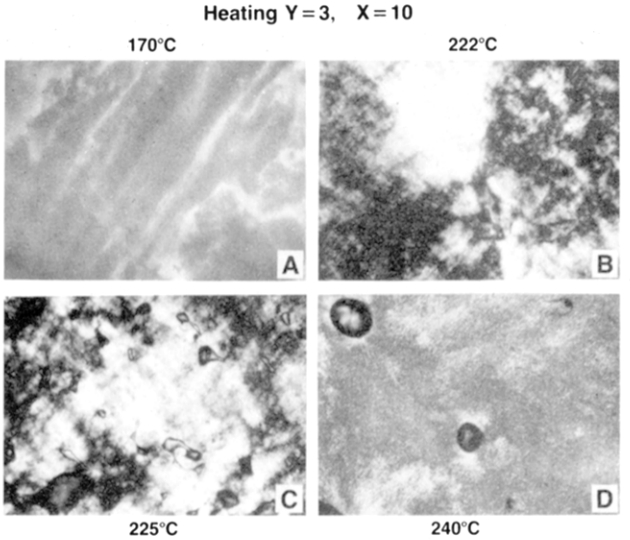


Figure 2. Cross-polarized light microscopy observations of $y = 3$, $x = 10$ upon heating. Magnification: 43×. Explanation in text.

Among the members of the $y = 9$ family, intense birefringence coupled with abrupt softening appeared throughout, but spontaneous flow was observed only in the case of $y = 9$ and $x = 7$, a deviation from the $x + y = 2n + 1$ rule. The concomitant existence of multiple transitions in the DSC heating scans with a birefringent flowing mass between them is taken to indicate the presence of thermotropic liquid crystallinity. Figure 3, for $y = 3$ and $x = 8$ at 503 K, is typical. Thus, we conclude that most of the poly(ester amides), with $y = 3$, 4, 5, and 9, exhibit mesomorphic behavior. The onset of spontaneous flow for $x + y = 2n + 1$ appears to indicate that more than one mesomorphic form may exist for these polymers.

DSC scans of poly(ester amides) with $y = 3$ and $1 \leqslant x \leqslant 4$ reveal two major endotherms in the heating cycle and no transitions in the cooling cycle. In the case of poly(ester amides) with $y = 3$ and $5 \leqslant x \leqslant 8$, the DSC heating cycles reveal two major endotherms and an additional minor endotherm in some members. In the cooling cycle, there usually appears only one exotherm which is substantially supercooled relative to the uppermost major endotherm. Figure 4 is typical of all polymers with $10 \leqslant x \leqslant 14$. In it a complete sequence of heating, cooling, and reheating is shown for the poly(ester amide) $y = 3$, $x = 14$. Notice the minor transitions above ca. 210 °C in the heating cycles. It is obvious that the major and minor endotherms and exotherms in the heating cycles reproduce extremely well. In the cooling cycle, an abrupt ordering takes place at some supercooling relative to the major endotherm in the heating cycle. The presence of such supercooling is characteristic of transitions from the mesomorphic to the crystalline state, while the absence of supercooling is typical of mesomorphic to mesomorphic transitions.[4] In Figure 5, a magnified portion of the first heating cycle from Figure 4 is shown. The irreproducible minor transition at about 125 °C corresponds to a transition from a metastable C_1 crystalline form to a stable, C_2, crystalline modification. Above the uppermost major endotherm (ca. 200 °C), at least two reproducible minor exotherms are visible. The multiplicity and reproducibility of the upper minor transitions are more clearly visible in a magnified portion of two heating cycles in the DSC scan of the poly(ester amide) $y = 5$, $x = 14$, in Figure 6. Figures 4–6 are typical of all poly(ester amides) with $y \geqslant 3$ and $10 \leqslant x \leqslant 14$.

The crystallinity content of the poly(ester amides) was estimated by conventional X-ray procedures. The results for the pristine and several annealed polymers are pres-

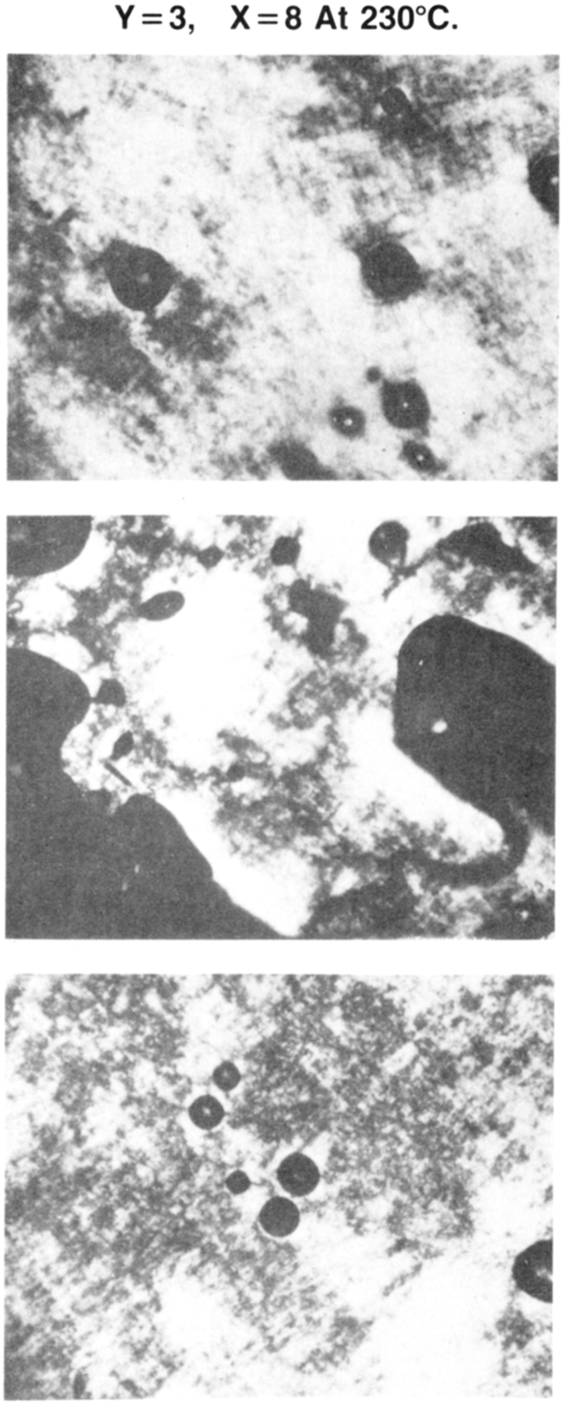


Figure 3. Fluid, intensely birefringent phase of $y = 3$, $x = 8$ at 230 °C observed by cross-polarized light microscopy. Magnification: 70×.

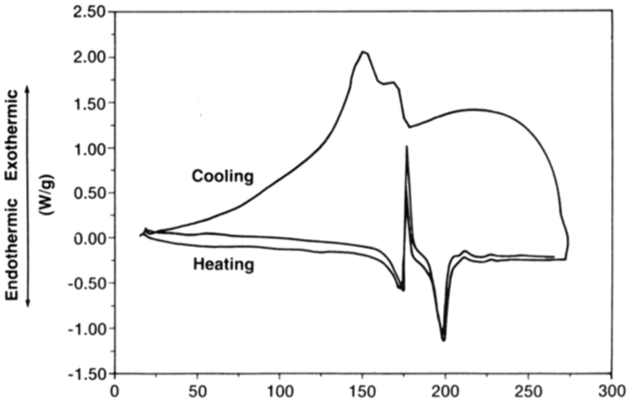


Figure 4. DSC scans of $y = 3$, $x = 14$. Complete heating, cooling, and reheating cycles.

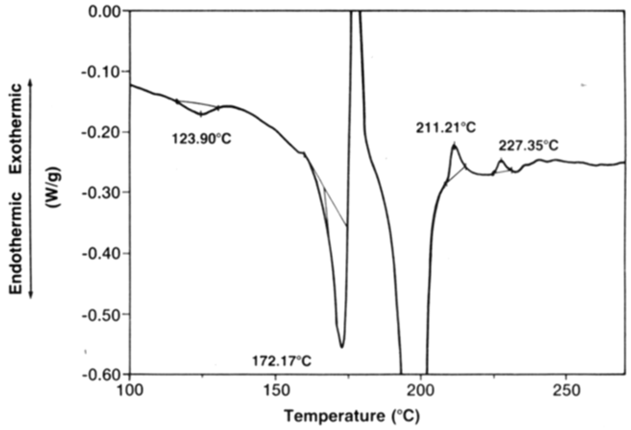


Figure 5. Magnified portion from the first heating cycle of the DSC scan in Figure 4.

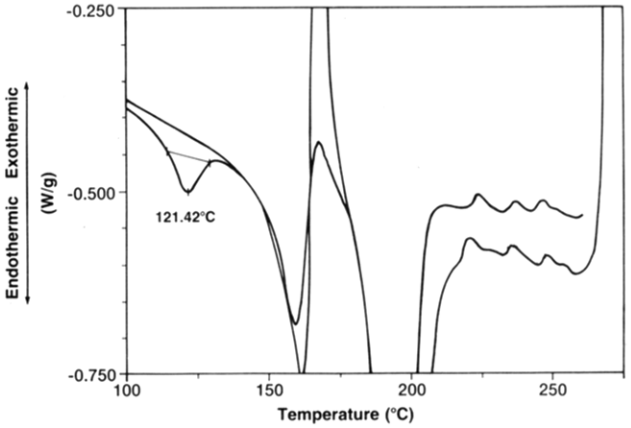


Figure 6. Highly magnified portion of two heating cycles in the DSC scan of poly(ester amide) $y = 5$, $x = 14$.

ented in Table I. The average crystallinity of all the pristine poly(ester amides) is 42%, and this number was used in all calculations where no individual crystallinity levels were available. Up to eight DSC scans were obtained for each polymer. Values of ΔH for each transition of each polymer were first averaged from all relevant scans. Then the estimates of $\Delta H°$ were obtained by normalizing to 100% crystallinity using either the tabulated individual crystallinity index of the particular polymer or the average of 42% crystallinity. All the reproducible transitions for all poly(ester amides) are tabulated in Table II, each with its transition temperature, T, in kelvin and the normalized heat of transition, $\Delta H°$, in kilojoules per mole. In addition to the first-order reproducible transitions, glass transition temperatures, T_g, are indicated when observed. Exothermic transitions observed by DSC during the cooling cycles are presented in the two right-hand columns of Table II. There were no observed endotherms during any of the cooling cycles. In almost all cases, no minor transitions were observed in the cooling cycles of the DSC scans, which may be comparable with the minor transitions upon heating. The development of ordered structures without DSC thermal transitions was reported several times in the literature.[5-9] It is, most likely, a consequence of relatively slow structure formation and the very small heats of transition associated with this structurization. The irreproducible C_1 to C_2 transitions mentioned above, which occur usually at around T_g + 75 K to T_g + 100 K, do not appear in the table. Values of the total heats of

Table I
Poly(ester amides): Crystallinity Determination by X-ray

polym				polym			
y	x	% crystal.	conditn	y	x	% crystal.	conditn
2	3	35 ± 2.5	pristine	4	3	38 ± 2.5	pristine
2	4	40 ± 2.5	pristine	4	4	38 ± 2.5	pristine
2	7	40 ± 2.5	pristine	4	5	30 ± 2.5	pristine
2	8	40 ± 2.5	pristine	4	6	32 ± 2.5	pristine
3	3	34.6 ± 1	pristine	4	7	30 ± 2.5	pristine
3	4	41.7 ± 1	pristine	4	8	38 ± 2.5	pristine
3	4	43.2 ± 1	annealed	4	10	40 ± 2.5	pristine
3	5	31.5 ± 1	pristine	4	11	33 ± 2.5	pristine
3	6	37.0 ± 1	pristine	5	11	41.1 ± 1	pristine
3	7	34.3 ± 1	pristine	5	11	40.7 ± 1	annealed
3	7	36.1 ± 1	pristine	5	14	48.8 ± 1	pristine
3	7	33.5 ± 1	annealed	5	14	53.5 ± 1	annealed
3	8	47.1 ± 1	pristine	9	3	38.8 ± 1	pristine
3	8	42.3 ± 1	annealed	9	4	42.4 ± 1	pristine
3	12	47.3 ± 1	pristine	9	7	43.5 ± 1	pristine
3	14	49.1 ± 1	pristine	9	8	42.4 ± 1	pristine
3	14	54.5 ± 1	annealed	9	11	40.4 ± 1	pristine
4	2	40 ± 2.5	pristine	9	12	40.0 ± 1	pristine

transition, ΔH°_{tot}, were obtained by summing up all the ΔH° of all reproducible endotherms in the heating cycles of the DSC scans, while neglecting the exotherms in the same heating cycles.

Now, when a thermotropic polymer during a heating cycle undergoes a series of first-order major and minor transitions, it is warranted to ask whether the minor transitions are characterized by small values of ΔH° with all or most of the polymer involved or whether the values of ΔH° are large but only a small fraction of the polymer participates in the minor transitions, resulting in small ΔH values. Since isothermal anneal at the transition temperature usually increases the fraction of polymer participating, it is expected that prolonged annealing at the peak temperatures of the minor exotherms and endotherms will increase the fraction of polymer being ordered in an exotherm and disordered in a higher endotherm. The poly(ester amides) $y = 3$, $x = 3$; $y = 3$, $x = 4$; $y = 3$, $x = 8$; $y = 3$, $x = 11$; $y = 3$, $x = 14$; $y = 5$, $x = 8$; $y = 5$, $x = 12$; and $y = 5$, $x = 14$ were kept isothermally in the DSC instrument and the hot-stage microscope at various transition temperatures for up to 90 min each. Usually, the lowest temperature for anneal was the uppermost major endotherm, and the highest anneal temperature was the uppermost minor transition below the isotropization temperature, T_i. These samples were all compared with the corresponding ones that underwent no isothermal annealing. No increase with anneal in the magnitude of any relevant transition was ever observed. This indicates that in the range of mesomorphic behavior of the poly(ester amides) with multiple thermal transitions, the magnitude of the transitions reflects the behavior of the whole or a major fraction of the polymeric sample and not only a small fraction of it. Hence, the major transitions in the mesomorphic interval have large ΔH° values per mole of repeat units, and the minor transitions have small ΔH° values. We are satisfied, therefore, that the values of ΔH° for all the transitions in Table II, estimated as described above, are reasonably close to the correct values for the fully ordered polymers. Furthermore, the constancy of the results indicates that at a heating rates of 10 K/min or less, equilibrium conditions are met or, at least, approached.

An examination of Table II shows that poly(ester amides) with $y = 3$ and $y = 5$ exhibit multiplicity of first-order transitions, while those with $y = 2$, most with $y = 4$, and those with $x = 20$ exhibit only a single endotherm, $T_m = T_i$. The most interesting polymers are those with $y = 3$ and $10 \leqslant x \leqslant 14$, $y = 5$ and $7 \leqslant x \leqslant 14$, and $y = 9$ and $x = 7$. All but two of these poly(ester amides) exhibit at least four endothermic transitions. Each of the poly(ester amides) with $y = 3$ and $10 \leqslant x \leqslant 14$ exhibits two major endotherms and two minor endotherms at higher temperatures. Mesomorphic behavior was observed among these polymers[1] at least in the interval from the uppermost major endotherm to T_i. The magnitudes of ΔH° for the major endotherms rest in the interval $18 \leqslant \Delta H^\circ \leqslant 75$ kJ/mol and the magnitudes of the minor endotherms in the range $0.9 \leqslant \Delta H^\circ \leqslant 2.4$ kJ/mol. In the case of poly(ester amides) with $y = 5$ and $8 \leqslant x \leqslant 14$, there exist per polymer at least two major endotherms and three minor endotherms at higher temperatures, with mesomorphicity present at least above the uppermost major endotherm. The magnitudes of the major endotherms fall in the interval $9.7 \leqslant \Delta H^\circ \leqslant 99$ kJ/mol. The magnitudes of the minor endotherms fall in the range from very very small to not higher than $\Delta H^\circ = 1.35$ kJ/mol. From the number of the minor transitions it is assumed that in polymers with $y = 5$ there exists one more mesophase than in their analogues with $y = 3$. Comparison of the heats of the minor transitions with the compilation of Kelker and Hatz[2] indicates these transitions to involve at least one mesophase. It is possible that the uppermost minor transition is nematic/isotropic and the penultimate is a smectic/nematic phase change. From the major transitions in these polymers, the uppermost is expected to be a crystalline/smectic phase transition. A different pattern is expected in the case of polymers exhibiting several major endotherms and no minor ones. In this case, we believe the highest or the second-highest major transition involves a change into a mesomorphic state. We are not certain whether this phase is smectic or nematic, nor are we sure whether the lower temperature phase is crystalline or smectic. Firm assignment of specific transitions of individual poly(ester amides) requires additional work, but the generalizations indicated above appear to be supported by the DSC scans, optical microscopy, and X-ray studies at variable temperatures and on quick-quenched and oriented samples.[1]

In Table III are presented the values of ΔH°_{tot} based on the individual crystallinities listed in Table I for the pristine poly(ester amides). Also presented in Table III are the values of ΔH°_c calculated by the group-additivity procedure of Van Krevelen and Hoftyzer[10] for 100% crystalline polymers:

$$\Delta H^\circ_c\ (\mathrm{kJ/mol}) = 41.8 + 3.76(x + y) \qquad (1)$$

Values of ΔH°_{tot} calculated on the basis of an average 42% crystallinity for all the polymers in Table II are presented in Table IV. Also are shown the values of ΔH°_c for all the poly(ester amides) calculated by following the relationship

$$\Delta H^\circ_c\ (\mathrm{kJ/mol}) = 46 + 3.89(x + y) \qquad (2)$$

developed by Manzini et al.[11] for 100% crystalline poly(ester amides) showing a single $T_m = T_i$ point.

A look in Table III immediately shows a good agreement between the values of ΔH°_{tot} and ΔH°_c. Turning to Table IV, one finds that the values of ΔH°_{tot} from Table III are also in good agreement with the values of ΔH°_c in Table IV. Note, however, that the values of ΔH°_{tot} from Table IV are not in such good agreement with the calculated ΔH°_c values in both Tables III and IV. The largest deviations appear to be in cases where the actual percent crystallinity was far different from the averaged 42% used in the calculations of all ΔH°_{tot} in Table IV. A similar difference in accuracy in the estimates of ΔH° exists in Table II, where the values calculated on the basis of

Table II[a]
Thermal Transitions of Poly(ester amides)

	polym				heating transitns																						cooling transitns			
					endo		exo		endo		exo		endo		exo		endo		exo		endo		exo		endo		exo		exo	
no.	y	x	MW	T_g	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°	T	ΔH°
1	2	3	396																						555	62.1				
2	2	4	410																						596	66.4				
3	2	7	452																						543	70.1				
4	2	8	466																						563	78.5				
5	2	14	550																						526	105.2	458	130		
6	3	1	382																		442	29.4			471	31.6				
7	3	2	396																		494	1.2			531	65.0				
8	3	3	410	383									434	6.2			468	19.1	471	19.3	505	26.4	507	26.4	522	16.0	460	19.1	471	19.1
9	3	4	424	390													512	33.6	523	33.5	534	36.1			554	6.2	503	67.0		
10	3	5	438																		494	75.2					473	38.1		
11	3	6	452														497	43.0			509	34.1					486	39.3		
12	3	7	466	345													433	36.4	444	36.4	478	43.0					444	VVS		
13	3	8	480	350													489	64.5			500	19.7	518	VVS	523	VVS				
14	3	10	508										449	18.0	458	18.0	481	70.0	488	2.1	493	2.1	513	1.3	513	1.3	463	42.8		
15	3	11	522	335									436	38.7	443	38.7	471	53.1	493	2.2	502	2.2	511	1.1	515	1.1				
16	3	12	538										449	31.5	453	33.4	478	63.1	493	2.4	502	2.4	508	0.9	513	0.9	428	12.2		
17	3	14	564	335									446	26.3	450	28.0	473	75.3	484	2.4	495	2.4	501	1.0	508	1.0	425	59.9	448	28.0
18	3	20	648																						438	131.8	418	126.1		
19	4	2	410																						555	65.6				
20	4	3	424																						541	70.2				
21	4	4	438																						568	72.7				
22	4	5	452														472	10.7	481	8.0	494	33.4			499	33.3				
23	4	6	466																						525	79.7				
24	4	7	480																		461	57.7			479	25.2				
25	4	8	494																						507	87.4				
26	4	10	522																						494	96.9				
27	4	11	538																		452	28.7	460	10.9	474	72.5				
28	4	14	578																		476	47.2	481	46.9	492	65.4	455	58.6		
29	5	3	438	350															446	31.0	484	63.2	NV		515	6.8	NV			
30	5	4	452																		527	33.8	NV		540	41.0	NV			
31	5	5	466	340																	430	12.8	436	12.8	476	66.4	NV			
32	5	6	480	340															443	8.5	495	78.9	NV		569	4.6	NV			
33	5	7	494	360													429	39.3	435	39.3	463	48.5	483	4.5	490	VVS	NV			
34	5	8	508										435	14.9	442	14.9	489	76.7	506	0.5	522	VVS	525	0.5	535	VVS	410			
35	5	10	536						433	9.7	440	9.7	481	88.7	502	0.6	516	0.6	520	0.6	530	0.6	533	0.6	536	0.4	NV			
36	5	11	550		430	46.9	435	46.9	453	32.8			455	20.8	465	1.0	481	1.0	485	0.7	494	0.7	496	0.5	500	VVS	400			
37	5	12	564						427	10.5	434	10.8	469	92.7	493	1.3	507	0.9	510	0.9	518	0.9	522	0.9	537	1.4	NV			
38	5	14	592		435	14.9	443	4.9	472	99.0	488	0.6	498	0.6	504	0.6	508	0.6	516	0.6	519	0.4	522	0.2	526	0.2	445	139.4	483	2.0
39	5	20	676																						426	141.5	404	124.3		
40	9	3	494																		458	19.4	463	19.4	503	67.6	433	37.4		
41	9	4	508																		494	36.5	500	4.8	511	54.7	460	95.4		
42	9	7	550	340													397	39.0	404	50.8	430	50.8	NV		443	14.4	NV			
43	9	8	564																		406	9.7	413	19.4	457	97.5			383	19.4
44	9	11	606	330																	398	43.7	408	43.6	429	77.8	NV			
45	9	12	620																		406	30.2	413	30.2	444	95.4			383	30.2
46	9	14	648																		410	15.0	414	15.0	445	119.4	395	14.7	414	14.7

[a] NV = none visible in DSC scans; VVS = very very small.

Table III
Poly(ester amides): $\Delta H°_{tot}$ Based on Individual Crystallinities in Table I and $\Delta H°_c$ Calculated According to Group Additivity Procedures

polym				polym			
y	*x*	$\Delta H°_c$	$\Delta H°_{tot}$	*y*	*x*	$\Delta H°_c$	$\Delta H°_{tot}$
2	3	60.61	62.1	4	7	83.18	82.9
2	4	64.37	66.4	4	8	86.94	87.4
2	7	75.66	70.1	4	10	94.47	96.9
2	8	79.42	78.5	4	11	98.23	101.2
2	14	101.99		4	14	109.52	
3	1	56.85		5	3	71.90	
3	2	60.61		5	4	75.66	
3	3	64.37	67.6	5	5	79.42	
3	4	68.13	69.9	5	6	83.18	
3	5	71.90	75.2	5	7	86.94	
3	6	75.66	77.0	5	8	90.71	
3	7	79.42	79.4	5	10	98.23	
3	8	83.18	84.2	5	11	101.99	102.1
3	10	90.71		5	12	105.75	
3	11	94.47		5	14	113.28	115.7
3	12	98.23	98.0	5	20	135.85	
3	14	105.75	105.0	9	3	86.94	86.9
3	20	128.33		9	4	90.71	91.2
4	2	64.37	65.6	9	7	101.99	104.2
4	3	68.13	70.2	9	8	105.75	107.2
4	4	71.90	72.7	9	11	117.04	121.5
4	5	75.66	77.3	9	12	120.80	125.5
4	6	79.42	79.7	9	14	128.33	

Table IV
Poly(ester amides): $\Delta H°_{tot}$ Based on Averaged 42% Crystallinity for All Polymers and $\Delta H°_c$ Calculated According to Manzini et al.

polym				polym			
y	*x*	$\Delta H°_c$	$\Delta H°_{tot}$	*y*	*x*	$\Delta H°_c$	$\Delta H°_{tot}$
2	3	65.45	51.8	4	7	88.79	116.1
2	4	69.34	63.2	4	8	92.68	96.5
2	7	81.01	66.7	4	10	100.46	101.7
2	8	84.90	74.8	4	11	104.35	128.9
2	14	108.24	105.2	4	14	116.02	112.5
3	1	61.56	61.0	5	3	77.12	70.0
3	2	65.45	66.1	5	4	81.01	74.8
3	3	69.34	55.7	5	5	84.90	79.2
3	4	73.23	69.9	5	6	88.79	83.5
3	5	77.12	56.4	5	7	92.68	87.8
3	6	81.01	87.4	5	8	96.57	92.1
3	7	84.90	63.4	5	10	104.35	100.0
3	8	88.79	75.1	5	11	108.24	104.2
3	10	96.57	91.4	5	12	112.13	106.4
3	11	100.46	95.1	5	14	119.91	99.6
3	12	104.35	110.4	5	20	143.25	141.5
3	14	112.13	122.8	9	3	92.68	80.3
3	20	135.47	131.8	9	4	96.57	91.2
4	2	69.34	62.4	9	7	108.24	104.2
4	3	73.23	77.5	9	8	112.13	107.2
4	4	77.12	80.4	9	11	123.80	121.5
4	5	81.01	108.3	9	12	127.69	119.2
4	6	84.90	104.6	9	14	135.47	134.5

crystallinity levels from Table I are more accurate than those calculated on the basis of an averaged 42% crystallinity.

The generally good agreement between $\Delta H°_{tot}$ and $\Delta H°_c$ holds for all the poly(ester amides), independently of whether the polymer undergoes only one or several reproducible first-order transitions. This is especially clear in Table II. When the $\Delta H°$ values from all endotherms of a given poly(ester amide) are added up, the value of its $\Delta H°_{tot}$ falls nicely in the range of expectation and close to the calculated $\Delta H°_c$. The conclusion is that the total heat of transitions, going from the crystalline solid to the isotropic melt, is constant for each poly(ester amide). When there exists only one transition, $T_m = T_i$, all the heat of transitions is consumed in a single transition, $\Delta H°_{tot} = \Delta H°_m$. If there exist several transitions between the crystal and the isotropic melt, then $\Delta H°_{tot}$ is divided among all the transitions and no extra heat is added to the total. On its way from the crystal to the isotropic melt, the polymer is, simply, "melting in stages".[12]

The magnitudes of $\Delta H°_{tot}$ determined for our poly(ester amides) are in very good agreement with expectations[10] and with values determined for similar poly(ester amides) by Manzini et al.[11] but appear to be significantly larger than most $\Delta H°_{tot}$ reported in the literature for thermotropic polymeric liquid crystals[3,13-17] as well as for common nonmesomorphic polymers.[10,18] Many of these differences can simply be explained as a consequence of the molecular weight per repeat unit of our poly(ester amides) generally being much larger than that of most polymers in the literature. We further believe that poor crystal packing and high level of crystalline imperfections[19,20] are possibly important reasons for the rather small $\Delta H°_{tot}$ of many of the liquid-crystalline polymers in the literature. It is important to recognize, however, that quite a few mesogenic substances possess heats of transitions similar in magnitude to the major transitions of poly(ester amides) having multiple endotherms listed in Table II. Among these one finds, for example, the large compilation in the *Handbook of Liquid Crystals*,[2] several Schiff-base liquid crystals,[21] and, especially important, the hydrogen-bonded *n*-alkyl gluconamide family of liquid crystals.[22]

Finally, it is instructive to compare the melting temperatures of the intermolecularly hydrogen-bonded poly(alkyleneterephthalamides)[23] with those of the comparable poly(alkylene terephthalates)[24] where no H-bonds exist and with poly(esteramides) where intermolecular H-bonds operate only between the amide residues and do not involve the ester groups.[1] The poly(ester amides) were prepared in two fashions. In one case,[6,25] they were prepared by high-temperature melt polycondensation, resulting in somewhat randomized polymers with modest to low crystallinity index, with each such polymer having only

Table V
Melting Points of Comparable Polyamides, Polyesters, and Poly(ester amides)

methylene groups per aromatic ring in chain	polyamide[23] T_m, K	polyester[24] T_m, K	melt-polymerzd[11,25] poly(ester amides)		soln-polymerzd[1] poly(ester amides)	
			$y + x$	T_m, K	$y + x$	T_m, K
2	728	538	4 + 6	523	2 + 3	555
3	672	506	6 + 6	520	2 + 4	596
4	709	505	6 + 6	526	2 + 7	543
5	626	407	4 + 7	506	2 + 8	563
6	644	427	6 + 7	506	2 + 14	526
8		405	4 + 8	506	4 + 2	555
9		358	6 + 8	505	4 + 3	541
10		402	2 + 12	517	4 + 4	568
			6 + 12	487	4 + 6	525
			12 + 12	470	4 + 8	507
					4 + 10	494

a single melting point, $T_m = T_i$, with no tendency toward mesomorphic behavior. The randomization is caused by high-temperature driven transesterification and transamidation reactions. In the second case, we have synthesized the poly(ester amides) from diacids and preformed (diaminobenzoyl)alkanes in solution at modest or low temperatures where no randomization took place.[1] For the purpose of comparison, we chose from these poly(ester amides) only the ones with $y = 2$ and $y = 4$ characterized by a single melting point, $T_m = T_i$. The results are presented in Table V. From the table it is obvious that the polyamides melt at about 200 K higher than the comparable polyesters. Comparison with the poly(ester amides) indicates that on the average the melting points of these polymers reside about halfway between those of the comparable polyamides and polyesters. It should be noted that the melting points of poly(ester amides) prepared by melt polycondensation are only a degree or two lower than those of the corresponding poly(ester amides) prepared in solution at much lower temperatures. The crystallinity levels are, however, significantly different. In the case of the highly regular solution-polymerized poly(ester amides), the crystallinities average to 42%, while in the case of the somewhat random melt-polymerized analogues the crystallinities were as low as 5% and never higher than about 25%.

Conclusions

When normalized to 100% crystallinity, the total heats of transition, ΔH°_{tot} of the poly(ester amides) are in good agreement with comparable experimental literature values[11] and with values calculated according to the group additivity method.[10] Poly(ester amides) with $y = 2$ and many of those with $y = 4$ exhibit a single sharp endotherm with large $\Delta H^\circ = \Delta H^\circ_{tot}$ where the crystalline polymer melts into an isotropic melt, $T_m = T_i$. Most other poly(ester amides) exhibit a multiplicity of reproducible first-order endotherms, indicating a process of melting in stages. Polymers with $y = 3$ and $y = 5$ and $8 \leqslant x \leqslant 14$ each exhibits several major endotherms followed by several minor endotherms at higher temperatures. The heats of transition of the minor endotherms are small, indicating transitions from one mesomorphic phase to another, followed by a final transition from a liquid-crystalline phase to the isotropic melt. In total, up to four mesomorphic states may be present in some of these poly(ester amides). X-ray work in the previous paper[1] indicates that at least one of these phases is a smectic C or a twisted smectic C phase. However, the exact nature of all these phases was not elucidated as of now. Poly(ester amides) with $x \leqslant 8$ and $y = 3$ or $y = 5$, as well as those with $y = 9$ and some with $y = 4$, exhibit two or three major endotherms in their heating cycle. The nature of the phases is not yet ascertained, but the optical observations and the magnitudes of the heats of transitions involved combine to suggest that between the crystalline and isotropic states there exist at least one mesomorphic state, probably a high viscosity and low mobility smectic phase, and another one with much lower viscosity.

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Registry No. $(HO_2C(CH_2)_3CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (copolymer), 114677-07-5; $(HO_2C(CH_2)_3CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (SRU), 114677-80-4; $(HO_2C(CH_2)_4CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (copolymer), 114677-08-6; $(HO_2C(CH_2)_4CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (SRU), 114677-81-5; $(HO_2C(CH_2)_7CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (copolymer), 114677-09-7; $(HO_2C(CH_2)_7CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (SRU), 114677-82-6; $(HO_2C(CH_2)_8CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (copolymer), 114677-10-0; $(HO_2C(CH_2)_8CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (SRU), 114677-83-7; $(HO_2C(CH_2)_{14}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (copolymer), 114677-11-1; $(HO_2C(CH_2)_{14}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_2O_2CC_6H_4NH_2)$ (SRU), 114677-84-8; $(HO_2CCH_2CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-13-3; $(HO_2CCH_2CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-86-0; $(HO_2C(CH_2)_2CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-14-4; $(HO_2C(CH_2)_2CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-87-1; $(HO_2C(CH_2)_3CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-15-5; $(HO_2C(CH_2)_3CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-88-2; $(HO_2C(CH_2)_4CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-16-6; $(HO_2C(CH_2)_4CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-89-3; $(HO_2C(CH_2)_5CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-17-7; $(HO_2C(CH_2)_5CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-90-6; $(HO_2C(CH_2)_6CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-18-8; $(HO_2C(CH_2)_6CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-91-7; $(HO_2C(CH_2)_7CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-19-9; $(HO_2C(CH_2)_7CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-92-8; $(HO_2C(CH_2)_8CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-20-2; $(HO_2C(CH_2)_8CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-93-9; $(HO_2C(CH_2)_{10}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-21-3; $(HO_2C(CH_2)_{10}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-94-0; $(HO_2C(CH_2)_{11}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-22-4; $(HO_2C(CH_2)_{11}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-95-1; $(HO_2C(CH_2)_{12}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-23-5; $(HO_2C(CH_2)_{12}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-96-2; $(HO_2C(CH_2)_{14}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-24-6; $(HO_2C(CH_2)_{14}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-97-3; $(HO_2C(CH_2)_{20}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (copolymer), 114677-25-7; $(HO_2C(CH_2)_{20}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_3O_2CC_6H_4NH_2)$ (SRU), 114677-98-4; $(HO_2C(CH_2)_2CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-26-8; $(HO_2C(CH_2)_2CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114677-99-5; $(HO_2C(CH_2)_3CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-27-9; $(HO_2C(CH_2)_3CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-00-1; $(HO_2C(CH_2)_4CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-28-0; $(HO_2C(CH_2)_4CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-01-2; $(HO_2C(CH_2)_5CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-29-1; $(HO_2C(CH_2)_5CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-02-3; $(HO_2C(CH_2)_6CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-30-4; $(HO_2C(CH_2)_6CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-03-4; $(HO_2C(CH_2)_7CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-31-5; $(HO_2C(CH_2)_7CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-04-5; $(HO_2C(CH_2)_8CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-32-6; $(HO_2C(CH_2)_8CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-05-6; $(HO_2C(CH_2)_{10}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-33-7; $(HO_2C(CH_2)_{10}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-06-7; $(HO_2C(CH_2)_{11}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-34-8; $(HO_2C(CH_2)_{11}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-07-8; $(HO_2C(CH_2)_{14}CO_2H)(4,4'\text{-}H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (copolymer), 114677-35-9; $(HO_2C\text{-}$

$(CH_2)_{14}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_4O_2CC_6H_4NH_2)$ (SRU), 114678-08-9; $(HO_2C(CH_2)_3CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-36-0; $(HO_2C(CH_2)_3CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-09-0; $(HO_2C(CH_2)_4CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-37-1; $(HO_2C(CH_2)_4CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-10-3; $(HO_2C(CH_2)_5CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-38-2; $(HO_2C(CH_2)_5CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-11-4; $(HO_2C(CH_2)_6CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-39-3; $(HO_2C(CH_2)_6CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-12-5; $(HO_2C(CH_2)_7CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-40-6; $(HO_2C(CH_2)_7CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-13-6; $(HO_2C(CH_2)_8CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-41-7; $(HO_2C(CH_2)_8CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-14-7; $(HO_2C(CH_2)_{10}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-42-8; $(HO_2C(CH_2)_{10}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-15-8; $(HO_2C(CH_2)_{11}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-43-9; $(HO_2C(CH_2)_{11}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-16-9; $(HO_2C(CH_2)_{12}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-44-0; $(HO_2C(CH_2)_{12}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-17-0; $(HO_2C(CH_2)_{14}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-45-1; $(HO_2C(CH_2)_{14}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-18-1; $(HO_2C(CH_2)_{20}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (copolymer), 114677-46-2; $(HO_2C(CH_2)_{20}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_5O_2CC_6H_4NH_2)$ (SRU), 114678-19-2; $(HO_2C(CH_2)_3CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-48-4; $(HO_2C(CH_2)_3CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114678-20-5; $(HO_2C(CH_2)_4CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-49-5; $(HO_2C(CH_2)_4CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114678-21-6; $(HO_2C(CH_2)_7CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-50-8; $(HO_2C(CH_2)_7CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114678-22-7; $(HO_2C(CH_2)_8CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-51-9; $(HO_2C(CH_2)_8CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114678-23-8; $(HO_2C(CH_2)_{11}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-52-0; $(HO_2C(CH_2)_{11}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114678-24-9; $(HO_2C(CH_2)_{12}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-53-1; $(HO_2C(CH_2)_{12}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114691-78-0; $(HO_2C(CH_2)_{14}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (copolymer), 114677-54-2; $(HO_2C(CH_2)_{14}CO_2H)(4,4'-H_2NC_6H_4CO_2(CH_2)_9O_2CC_6H_4NH_2)$ (SRU), 114678-25-0.

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