

Thermal properties of poly- ϵ -caprolactam and copolyamides based on ϵ -caprolactam

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Abstract The copolyamides consisting of ϵ -caprolactam and 6.1–24.5 wt.% of nylon salt prepared from adipic acid and 1-(2-aminoethyl) piperazine were synthesized. Physical and thermal characteristics of polyamide 6 and the copolyamides were compared. Nylon salt does not influence the polyreaction equilibrium so it is possible to prepare the copolyamides with high molecular weight and with the content of low-molecular compounds comparable with that of pure PA 6. Melting temperatures of the copolyamides are lower in comparison with PA 6 and decrease proportionally to the amount of the nylon salt. The thermal stability of the copolyamides is good and equal to that of PA 6. The melting enthalpies indicate that the process of crystallization of the copolyamides is influenced by the time of crystallization and the amount of comonomer present. Longer time of the crystallization assures higher degree of crystallization. The kinetics and the level of crystallization are positively influenced by the mobility of copolyamide segments mainly up to 10 wt.% of comonomer.

Keywords ϵ -Caprolactam · Adipic acid · 1-(2-Aminoethyl) piperazine · Copolyamides · Thermal properties

Introduction

Commercial polymers are often modified with additives and new polymer materials are obtained with some better properties. Knowledge of characteristics of compounds used as additives to fibre-forming semicrystalline polymers is important. Copolymers are able to improve efficiently many properties, including thermal ones [1, 2]. Copolyamides based on ϵ -caprolactam with a functional comonomer can be mainly applied as additives especially for poly- ϵ -caprolactam—PA 6 [3, 4].

Among others, DSC method is suitable for determination of the content, thermal stabilities and glass transition temperatures of the components constituting the block polyamide 6-block-polybutadiene copolymer [5].

DSC and DMTA revealed that multiblock copolymers poly(ester-blockamide)s and poly(amide-blockamide)s with the same type of oligoamide soft block and oligoester hard block behaved as thermoplastic elastomers [6].

Addition of poly(amino-ether) with molecular structure similar to PA 6 form the blends with two phases; one comprised an almost pure polyamide phase and a poly(amino-ether) phase rich phase in which significant amounts of polyamide were miscibilized [7].

DSC analysis showed that the addition of chemically related biopolymer, *Bombyx mori*, (silk fibroin) to PA 6 caused a decrease in the crystallization temperature, melting temperature of the lowest melting crystals and the crystallinity of PA 6 [8].

Properties of polyamides depend on their chemical structure. According to DSC measurements semicrystalline polyamides can form crystalline and even two non-crystalline phases, i.e. mobile-amorphous phase and rigid-amorphous phase [9].

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Miscibility of two similar polyamides—PA 6 and PA 66 is limited and occurs in the interval when concentration c of PA 66 in blends $0.8 \leq c \leq 0.15$ [10].

DSC experimental results indicated that in blends of PA 6 and PA 6 modified with dimethyl-5-sulfoisophthalate sodium salt miscible domains are easily formed and these two polymers were proven to be a compatible system [11].

Crystallization of PA 6 in the blends with Biopol D600G is faster and results in increasing of the crystallization grade of polyamide phase comparing to its pure state [12].

The interactions between homopolyamide PA 6 and block copolyamide containing long ϵ -caprolactam segments [13], enable the preparation of a blend with better compatibility and improved properties of blended products, e.g., fibres. Block copolymers can form at least two types of crystallites and two or more peaks indicate various crystallites of different sizes and levels of perfection [14].

Homopolymer poly- ϵ -caprolactam contains some crystalline portion as a consequence of the regular spatial order of its macromolecules and intermolecular bonds as well. Due to copolyreaction, longitudinal disorder and reduced crystallinity result as a rule. In certain cases, however, the crystallinity is not reduced because the segment of the comonomer is similar in size to that which is being replaced. In the case of heteropolyamide from dicarboxylic acid and diamine like PA 66 from adipic acid and hexamethylenediamine, both components can be changed. For example, terephthalic acid with a length of 0.59 nm yields polyamides isomorphous with those of adipic acid with a segment of 0.63 nm because of their similar segment lengths [15]. Thus, copolymers of PA 66 and PA 6T are crystalline and do not have an eutectic in the melt temperature–composition curve. In contrast, when PA 610 is copolymerized with PA 6T, the eutectic effect is marked [16].

Comparison of chemical structures and the length of ϵ -caprolactam and 1-(2-aminoethyl) piperazine molecules, AN2, with those of adipic and terephthalic acids show that the segments of all the monomers are very similar concerning their length. This presumes the isomorphous and crystalline character of copolyamides containing ϵ -caprolactam and nylon salt AN2 consisting of adipic acid (A) and 1-(2-aminoethyl) piperazine (N2). Derivatives of piperazine in macromolecules prevent UV degradation [17] and improve thermal stability and dyeability [18]. In addition, the molecule of 1-(2-aminoethyl) piperazine is not symmetrical, so there is a possibility to build segments with various arrangements in the copolyamide macromolecules and to obtain different crystallites as well [3].

Usually, the higher the amount of minor comonomer, the higher is the probability of a lower arrangement of the macromolecules and the possibility of decreasing the level of crystallization as well. This is valid in the case of random copolymers and in situations when the minor

comonomer cannot cocrystallize, i.e. its length and spatial arrangement is not close to that of a major comonomer. In the case of block copolymers, the situation would be different and a higher amount of the minor comonomer enables the formation of longer segments of both comonomers and two types of crystallites as well.

A minor comonomer with bulky piperazine rings brings about a lower amount of intermolecular bonds and a decrease in some characteristics (e.g., crystallinity, ΔH_m , T_m etc.)

The aim of this work was the preparation of copolyamides from ϵ -caprolactam and different amount of nylon salt consisting of adipic acid and 1-(2-aminoethyl) piperazine and the study of physical characteristics, thermal stability and thermal properties of the copolyamides prepared and the commercial homopolyamide PA 6.

Experiment

Material used:

ϵ -caprolactam, CL, Nylstar Slovakia, Humenné, poly- ϵ -caprolactam, PA 6, Nylstar Slovakia, Humenné, adipic acid p.a., A, Aldrich, 1-(2-aminoethyl) piperazine, N2, Aldrich, nylon salt, AN2, (from adipic acid, A, and 1-(2-aminoethyl) piperazine, N2),

copolyamides from ϵ -caprolactam and various amounts of comonomer AN2, designed by the concentration of the nylon salt AN2 at the beginning of polyreaction, e.g. KOPA 6.1 means that copolyamide contains 6.1 wt.% of AN2.

The copolyamides were prepared through a polyreaction in a melt under nitrogen atmosphere. Powdered ϵ -caprolactam and AN2 salt were mechanically mixed and put in a glass apparatus immersed in a thermostatted oil bath. The melting, homogenization and poly(addition–condensation) reaction was completed within 2 h with the exception of the sample containing the lowest amount of nylon salt (6.1 wt.%); in this case the polyreaction time was 3 h. The nylon salt acts as an activator of the polyaddition reaction of ϵ -caprolactam so the longer polyreaction time was used for copolyamide with the lowest amount of AN2. At the end of the polyreaction the copolyamides were poured onto a metallic plate and cut into granules.

Copolyamide samples were extracted in boiling water for 2 h, dried at 105 °C for 2 h. The amount of low molecular compounds was determined from the mass difference before and after extraction and drying.

The melting temperature, T_m , loss of mass and beginning of decomposition of PA 6 and copolyamides were evaluated by the differential thermal analysis using a

Derivatograph Q-1500D (MOM Budapest, Hungary) equipped with a computer program. The relative viscosity, η_r , (1 g of polymer/100 mL of H₂SO₄) and intrinsic viscosity, $[\eta]$, were determined viscosimetrically in a solution of H₂SO₄, anal. grade at 25 °C. The thermal properties, T_m , T_c , T_g , ΔH_m , and ΔH_c , were studied using the DSC 7 Perkin Elmer at 10 K min⁻¹ the heating and cooling rates. Three cycles were applied (heating–cooling–heating) for the study of thermal properties.

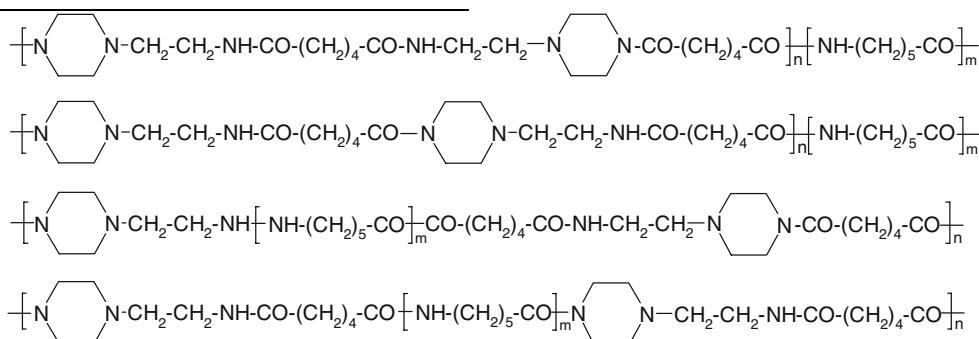
Results and discussion

Physical characteristics of PA 6 and copolyamides

Nylon salts from dicarboxylic acids and diamines have a catalytic influence on the polyreaction of ϵ -caprolactam. So a polyreaction with a sufficient amount of AN2 is much more rapid, and the molecular weight of the copolyamides, according to the relative viscosity, η_r , and intrinsic viscosity, $[\eta]$, are only a little lower in comparison with the homopolymer PA 6 (Table 1).

Melting temperatures T_{m1} and T_{m2} show (Table 2) that at least one value of T_{m1} is higher than the highest value of T_{m2} . This indicates the fact that long time of crystallization affects the level of crystallinity and, during the period from the synthesis to the first DSC measurement possible recrystallization of the former crystallites into crystallites with a more perfect arrangement with higher melting temperature can occur. During the second heating a splitting of peaks is observed (Fig. 1) but the highest part of crystallites is melted at the temperature nearest to the higher or single melting temperature from the first heating.

The splitting of T_m peaks at the first and mainly at the second heating indicates two or three crystalline modifications of PA 6 and copolyamides. According to ΔH_m values for each polymer, one of these modifications is predominant. This is not generally true in the case of the first heating, so it can be stated that after the primary crystallization, the second crystallization and the recrystallization can occur in a longer period. Owing to the asymmetrical structure of 1-(2-aminoethyl) piperazine, the copolyamide chain structure is irregular and it can contain various segments, which presents the possibility for more crystalline structures [3].



The amount of low molecular compounds for the pure homopolymer PA 6 depends on the temperature of the synthesis, and it is from an interval of 8–12 wt.%. The low molecular compounds of copolyamides KOPA 14–KOPA 24.5 is comparable with this value mainly at a higher concentration of comonomer AN2 (Table 1).

Thermal stability as the mass loss at a certain temperature and their beginning of decomposition as an intense deviation from the dependence $\Delta m = f(T)$ were evaluated. Thermal stability of the prepared copolyamides is comparable with that of the homopolymer poly- ϵ -caprolactam. The mass loss of all copolyamides, especially at higher temperatures used during melt processing, is at the same level as for the homopolymer PA 6 and the temperatures of beginning of decomposition are even higher than those for PA 6 (Table 1).

The melting temperatures T_{m2} of the major part of each copolyamide decrease linearly up to the amount of 14 wt.% of the comonomer AN2. At higher amounts this drop is higher (Table 2).

The temperatures of crystallization, T_c (Table 2) decrease as well: there are two temperatures T_c for some copolyamides. This fact corresponds with the above-mentioned asymmetrical structure of 1-(2-aminoethyl) piperazine and copolyamides as well. The depression of T_c supports the idea about the higher mobility of the copolyamide macromolecules with a higher amount of the comonomer, i.e., with a less ordered structure, and coheres with a depression in the glass temperature T_g .

Glass temperature, T_g , of copolymers is always lower in comparison with homopolymer as a consequence of lower cohesive energy between macromolecules of copolymer.

Table 1 Physical characteristics of PA 6 and copolyamides using the Derivatograph

Polymers	TP (h)	T_m (K)	LMC (wt.%)	$[\eta]$ (l kg ⁻¹)	η_r	Loss of mass, wt.% at K					BD (K)
						373	473	523	573	623	
PA 6 ^a	>16	496	1.2 ^b	92	2.88	4.7	8.7	9.5	10.2	11.9	603
KOPA 6.1	3	483	15.4	72	2.07	4.3	9.1	9.7	10.9	13.2	633
KOPA 9.6	2	479	15.1	79	2.11	5.1	7.8	8.2	9.7	11.2	643
KOPA 14	2	471	9.9	81	2.18	3.8	9.6	10.6	11.3	13.4	603
KOPA 20.2	2	460	9.8	82	2.2	3.3	8.5	9.0	9.7	12.1	618
KOPA 24.5	2	451	8.2	85	2.34	3.9	8.9	9.8	10.8	14.7	599

TP time of polyreaction, BD beginning of decomposition

^a Commercial product

^b Residual value after extraction by the producer, before extraction it is about 12 wt.%

Table 2 Partial thermal characteristics of PA 6 and copolyamides

Molar ratio CL/AN2	Polymer	(1) Heating			Cooling		(2) Heating		
		T_{g1} (K)	T_{m1} (K)	ΔH_{m1} (J g ⁻¹)	T_c (K)	ΔH_c (J g ⁻¹)	T_{g2} (K)	T_{m2} (K)	ΔH_{m2} (J g ⁻¹)
–	PA 6	319	496.7	76.1	453.4	66.1	324.5	453.9	1.4
30/1	KOPA 6.1	302	479.9	43.9	443.2	57.9	319.1	445.9	0.8
			487.1	31.5				473.9	8.9
								485.7	40.3
20/1	KOPA 9.6	302	476.6	44.6	434.0	53.2	321.2	435.8	0.85
			482.1	26.6				467.9	7.8
								480.2	37.9
14/1	KOPA 14	302			419.2	10.5	321.4	420.5	0.6
			473.1	59.8				434.7	31.8
9/1	KOPA 20.2	302	460.2	34.8	397.0	36.1	321.4		
			461.7	18.0					
7/1	KOPA 24.5	302			370.9	0.9	321.4	363.2	–9.2
			451.0	50.8				403.5	8.5

The presence of water has the same effect. If molecules of water are present in the sample the number of hydrogen bonds between amide groups decreases, another drop of cohesive energy is manifested and flexibility of the macromolecular segments increases. These two effects can contribute to the secondary crystallization and higher ΔH_{m2} values.

The presence of the comonomer AN2 is manifested by a substantial drop in the glass temperature, T_g , mainly in combination with the effect of moisture. All non-dried samples have their T_{g1} values equal and lower compared with PA 6. The drop of T_{g2} of the copolymers is much lower than drop of T_{g1} due to the absence of water.

Thermal characteristics of PA 6 and copolyamides

The first heating of all the copolyamides was realized several weeks after their synthesis. The value of ΔH_{m1} (Tables 2, 3)

expresses the melting enthalpy of the crystalline part formed during the solidification of the copolyamide melt at the end of the synthesis, i.e. primary crystallization plus the melting enthalpy of the crystalline part formed during the time from the synthesis to the first heating of the DSC measurement when the amorphous phase of copolyamides have enough time to crystallize and former crystallites could recrystallize to a more organized state. Therefore ΔH_{m1} values are much higher than ΔH_{m2} values.

Both ΔH_{m1} and ΔH_{m2} decrease with the amount of the minor comonomer and they are lower than these for PA 6, but a comparison shows that the ability to crystallize of all the copolyamides is rather high, mainly for the copolyamides with less than 10 wt.% of AN2 comonomer. The contribution of the secondary crystallization in the copolyamides is higher than that for PA 6, which indicates that the mobility of the copolyamide macromolecules is higher.

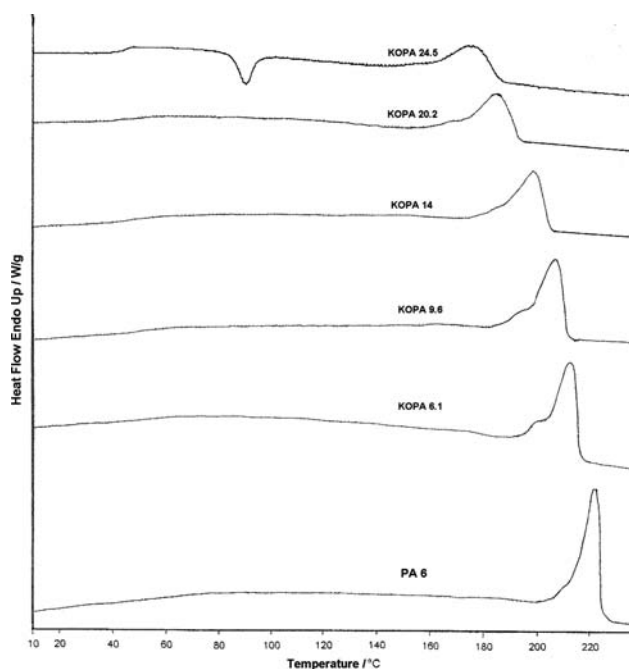


Fig. 1 Endotherms of PA 6 and copolyamides obtained at the second heating

The relatively low enthalpies ΔH_m of 100% crystalline homopolyamides PA 6 and PA 66, i.e. 190 and 200 J g⁻¹ respectively in comparison with, 100% crystalline polyethylene, i.e. 293 J g⁻¹, [19] suggest that strong hydrogen bonds are conserved partially in the polyamide melt, and only enthalpy of $-\text{CH}_2-$ groups interactions is consumed during the melting. Since the percentage of $-\text{CH}_2-$ groups in the polyamides is lower than in the polyethylene, ΔH_m values of the polyamides are lower than that for polyethylene. In the case where the nylon salt of adipic acid and 1-(2-aminoethyl) piperazine is incorporated instead of ϵ -caprolactam the percentage of $-\text{CH}_2-$ groups changes and depends on the amount of the AN2 comonomer in the copolyamides.

The uniform drop of both ΔH_{m1} and ΔH_{m2} values with a higher amount of the comonomer AN2 indicates a lower

amount of intermolecular bonds in the crystallites or a lower degree of crystallinity respectively. At $T = 90.6$ °C the KOPA 24.5 exhibits a negative ΔH_{m2} value equal to -9.2 J g⁻¹ (Fig. 1) and strongly reminds the polyethylene terephthalate and some binary and ternary copolyamides [13] with their so-called cold crystallization. From this point of view the existence of a random copolyamide, maybe with more regularly situated piperazine rings, could be assumed.

Both ΔH_{m1} and ΔH_{m2} values decrease with increasing amount of minor comonomer. ΔH_{m1} consists of two contributions: one of them expresses the primary crystallization occurring during cooling of the copolyamide melt after the synthesis, and the other one is the result of secondary crystallization during time between the synthesis and the first heating of DSC measurement. ΔH_{m2} is the melting enthalpy for crystallites formed during cooling after the first DSC heating. So the difference ($\Delta H_{m1} - \Delta H_{m2}$) indicates the contribution of secondary crystallization and it is higher for all the copolyamides (except for KOPA 20.2) than that for PA 6 which suggests a higher mobility of the copolyamide macromolecular segments.

The ΔS_m , ΔH_m and T_m values are mutually connected by the relationship:

$$\Delta S_m = \Delta H_m / T_m$$

The ΔS_m value expresses the difference between the entropy in the solid and molten states. In the molten state the macromolecules themselves can be considered as free, so the higher the value ΔS_m , the higher is the order of the system of macromolecules in the solid state. The opposite situation occurs when ΔS_m value is lower, and the transition of the system from a solid to molten state is connected with a lower change in the macromolecular arrangement, and fewer interactions in the solid state are present. From the above-mentioned relationship and the assumption that ΔH_m^0 values for 100% crystalline copolyamides are close to that for PA 6, it is possible to calculate the approximate value of ΔS_m . Despite, the impossibility of calculating the exact ΔS_m value if the polymer has more crystalline modifications

Table 3 Total thermal characteristics of PA 6 and copolyamides

Molar ratio CL/AN2	Polymer	(1) Heating			Cooling		(2) Heating			$\Delta H_{m1} - \Delta H_{m2}$ (J g ⁻¹)
		T_{m1} (K)	ΔH_{m1} (J g ⁻¹)	ΔS_{m1} (J K ⁻¹ g ⁻¹)	T_c (K)	ΔH_c (J g ⁻¹)	T_{m2} (K)	ΔH_{m2} (J g ⁻¹)	ΔS_{m2} (J K ⁻¹ g ⁻¹)	
–	PA 6	496.8	76.1	0.153	453.4	66.1	496.0	55.2	0.111	20.9
30/1	KOPA 6.1	487.2	75.4	0.155	443.2	57.9	485.8	50.0	0.103	25.4
20/1	KOPA 9.6	482.2	71.2	0.148	434.0	53.2	480.3	46.55	0.097	24.65
14/1	KOPA 14	473.2	59.8	0.126	434.7	42.3	471.7	38.8	0.082	21.0
9/1	KOPA 20.2	461.8	52.8	0.114	397.0	36.1	458.0	32.6	0.08	20.2
7/1	KOPA 24.5	451.1	50.8	0.113	403.5	9.4	449.3	29.5	0.066	21.3

(each with its own ΔH_m and T_m values), we can estimate the ΔS_m values (Table 3) rather well. The PA 6 with its high crystalline portion with a maximal macromolecular order exhibits the higher ΔS_m value. The ΔS_m values (Table 3) support the fact that copolyamides up to approximately 10 wt.% of the comonomer AN2 are nearly at the same level of molecular order as the PA 6.

From the point of view of macromolecular regularity and the number of intermolecular bonds, the prepared copolyamides can be divided into two groups:

- copolyamides with an amount up to 10 wt.% of comonomer AN2 are similar to PA 6 in their macromolecular arrangement, and their ability to crystallize is high, and copolyamides with a higher amount of comonomer AN2 and a lower crystallization ability.

Conclusion

Copolyamides containing polar atoms of nitrogen in piperazine cycle, based on ϵ -caprolactam are excellent, compatible additives for poly- ϵ -caprolactam (PA 6) and can be synthesized within a much shorter time in comparison with PA 6. Despite this fact their molar weights are comparable with that of PA 6. As a consequence of the comonomer effect the melting temperatures are lower and decrease proportionally to the amount of nylon salt AN2.

The thermal stability of all the copolyamides is very good and at least the same as for the PA 6.

The comonomer decreases the melting enthalpy ΔH_m of the copolyamides. The crystallization ability (according to ΔH_m) is high mainly for copolyamides with a lower amount of comonomer (up to 10 wt.%) and it is comparable with that for PA 6.

The comonomer affects kinetics of crystallization. The contribution of secondary crystallization for the copolyamides is higher than that for PA 6.

The temperature of the crystallization T_c of copolyamides decreases with the amount of comonomer.

Temperature of the glass transition T_g is affected only negligibly.

All above mentioned remarks confirm the assumption that these copolyamides are additives suitable for polyamides.

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References

1. Pielichowski M, Leszczynska A. TG-FTIR study of the thermal degradation of polyoxymethylene(POM)/thermoplastic polyurethane (TPU) blends. *J Therm Anal Calorim.* 2004;78:631–7.
2. Zhu G, Li Y, Yin J, Ling J, Shen Z. Thermal and crystalline properties of random copolymer of CL and DTC prepared by $\text{La}(\text{Oar})_3$. *J Therm Anal Calorim.* 2004;77:833–7.
3. Krištofič M, Marcinčin A, Borsig E. Preparation, properties and application of modified fibres with piperazine rings. *Polym Adv Technol.* 1999;10:179–86.
4. Krištofič M, Marcinčin A, Ujhelyiová A, Murárová A. Modification of PA 6 fibres with alkaline copolyamides. *Chem Pap.* 2000;54:53–8.
5. Brožek J, Budín J, Roda J. Thermal properties of block copolymers polyamide-6 – polybutadiene. *J Therm Anal Calorim.* 2007; 89:211–5.
6. Kozłowska A, Ukielski R, Piątek M. Thermal properties of multiblock thermoplastic elastomers with oligoamide soft blocks derived from dimerized fatty acid. *J Therm Anal Calorim.* 2006; 83:349–53.
7. Guerrica-Echevarria G, Eguizábal JI, Nazábal J. Synergistic mechanical behavior in new polyamide 6/poly(amino-ether) blends. *J Mater Sci.* 2002;37:4529–35.
8. Chen H, Hu X, Cebe P. Thermal properties and phase transition in blends of nylon-6 with silk fibroin. *J Therm Anal Calorim.* 2008;93:201–6.
9. Wunderlich B. Thermal properties of aliphatic nylons and their link to crystal structure and molecular motion. *J Therm Anal Calorim.* 2008;93:7–17.
10. Zhang GZ, Liu CQ, Yoshida H. Miscibility evaluation of nylon 66/nylon 6 blends investigated by crystalline dynamics. *J Therm Anal Calorim.* 2006;85:707–12.
11. Tsen W-C, Shu Y-C, Hsiao K, Jue Z-F. Physical properties of polyblends of polyamide 6 polymer with cationic dyeable polyamide 6 polymer. *J Polym Res.* 2004;11:189–94.
12. Haponiuk JT, Tercjak A. DSC studies on melting and crystallization of polyamide 6/biopol blends. *J Therm Anal Calorim.* 2000; 60:117–21.
13. Krištofič M, Marcinčin A, Ujhelyiová A. The DSC study of PA 6, polyamides and copolyamides. *J Therm Anal Calorim.* 2000;60: 357–69.
14. Löffler R, Navard P. DSC and X-ray studies of thermotropic four-monomer copolyester. *Macromolecules.* 1992;25:7172–9.
15. Edgar OB, Hill R. *J Polym Sci.* 1952;8:8, *Encyclopedia of Polymer Sci and Technology*, vol 10. NY: Wiley; 1969, p. 531.
16. Kaufmann MH, Mark HF, Mesrobian RB. *J Polym Sci.* 1954; 13:3, *Encyclopedia of Polymer Sci and Technology*, vol 10. NY: Wiley; 1969, p. 531.
17. Fr. Pat. 2 177 916, 1973.
18. Jpn. Kokai Tokkyo Koho JP 5821,424, in CA 99, P 72097d.
19. Brandrup J, Immergut EH. *Polymer handbook.* NY: John Wiley and Sons; 1989:V/19, V/112.