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The influence of chemical composition of amide block on the thermal properties and structure of terpoly(ester-*b*-ether-*b*-amide) elastomers

Summary — Multiblock terpolymers-(PBT-*b*-PTMO-*b*-PA12,10)$_n$- constituting the polymer systems, in which one of the three blocks (PBT) does not dissolve in PA12,10 block (hard phase) and, depending on its molecular weight is slightly soluble in PTMO block (soft phase), have been obtained. The DSC method was applied to investigate the thermal properties of these polymers and it was found that PBT block acts as an element that produces stiffness of -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- structure. Thus, this block causes deterioration of the elastic properties and leads to the formation of terpolymers showing the features of reinforced plastics. The terpolymers were compared with the previously described [5] -(PBT-*b*-PTMO-*b*-PA12)$_n$-. They are elastomers when the rigid PBT block's polymerization degree is in the range 4—7. Such a block — the rigid PBT block — dissolves in the hard phase of PA12 blocks and partly dissolves in the soft phase. So, it was found that even a small change in the chemical structure of the amide block influences significantly on the structure, phase separation and the properties of terpolymers. An analysis of the thermal properties of -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- confirms an argument that the block terpolymers show good elastic properties only in case when one of the blocks partly dissolves in the phases formed from the remaining blocks.

Key words: terpoly(ester-*b*-ether-*b*-amides), multiblock terpolymers, phase structure, mutual solubility of soft and hard blocks, elastic properties.

A polymeric material, which shows the ability to almost instant return to the original form after a large deformation and can be subjected to processing by analogous methods as the thermoplastic plastics is termed as the thermoplastic elastomer.

A part of the multiblock polymers of the type -$(A_xB_y)_n$-, and -$(A_xB_yC_z)_n$- can be included to a group of the thermoplastic elastomers. In order to be a good thermoplastic elastomer, the multiblock polymer should be characterized by:

1) Linear or slightly branched molecule (which determines the thermoplasticity).

2) Strictly defined differences in the chemical composition of the blocks termed as the flexible (soft) and rigid (hard) causing that these blocks exist in the different thermodynamical states at the same temperature (a thermodynamic condition of the phase separation enabling the formation of the heterophase structure).

3) An appropriate phases' composition of the system, which depends on the type of the blocks and their dimensions. This composition is responsible among others for the high-flexible features of copolymer and for a width of elasticity *"plateau"* at the temperature spectrum of the Young modulus (width of *"plateau"* determines a range of elastomer application).

4) An appropriate dispersion of the phases (microseparation, the possibility of nanostructures formation).

5) Adequate densities of the intermolecular and interphase links, which stabilize the nanostructure.

The fulfilment of conditions 3—5 is dependent on the mutual solubility of the respective blocks. In the systems of multiple repeating sequences (multiplication) of two blocks (multiblock copolymers) the structure is for the most part recognized [1—4]. These are heterogeneous two-phases systems with interface broadening (thin layer). Thus in the multiblock copolymers the blocks are insoluble each in other. Whereas the ternary systems (multiblock terpolymers), being the subject of our team investigation, are considered as significantly more complex. In these systems a layer termed as an intermediate phase (wide layer) may occur instead of the interface [5—9]. In Ukielski's - earlier works there was [5—7, 9] confirmed that the size of this intermediate phase would

Tabela 2. Wpływ modyfikacji PE-LD kwasem itakonowym wobec DCP na właściwości produktów

Table 2. Effect of PE-LD modification with itaconic acid, in the presence of DCP, on the properties of the products

Symbol próbki	Stężenie KI % mas.	Stężenie DCP % mas.	Naprężenie zrywające MPa	Wydłużenie względne przy zerwaniu %	Liczba żelowa % mas.
PE-LD	0	0	12,83	492	–
130	3	0,1	10,60	400	1,72
131		0,3	11,92	410	1,30
132		0,5	11,57	400	4,53
133		0,7	10,62	357	4,95
134		0,9	12,87	395	12,07
135		1,1	12,70	376	44,64
136	5	0,1	9,40	416	1,53
137		0,3	9,99	413	1,43
138		0,5	11,95	431	1,41
139		0,7	11,63	384	1,16
140		0,9	10,77	360	1,81
141		1,1	9,40	316	1,67
149	8	0,1	8,76	328	0,71
150		0,3	9,19	342	1,66
151		0,5	8,40	209	1,47
152		0,7	9,78	388	1,71
153		0,9	9,40	331	1,58
191		1,1	8,72	311	1,32
155	10	0,1	8,02	173	1,39
156		0,3	8,17	191	1,64
157		0,5	7,90	142	1,58
158		0,7	7,35	111	1,73
159		0,9	8,09	108	1,78
160		1,1	8,28	162	1,77
194	3	–	11,78	419	1,40
195	5	–	9,51	383	1,15
196	8	–	8,45	203	1,28

skutek oddziaływania podwyższonej temperatury, zwłaszcza w przypadku próbek zawierających DCP.

Jak wiadomo, nadtlenek dikumylu jako inicjator reakcji rodnikowych może sprzyjać nie tylko pożądanej reakcji szczepienia, lecz także procesowi termooksydacyjnej degradacji tworzywa; trzeba jednak zauważyć, że ten niekorzystny efekt ulega nieznacznemu pogłębieniu ze wzrostem udziału DCP (tabela 3), podczas gdy stopień szczepienia korzystnie rośnie wraz z tym udziałem (rys. 6).

Powyższa ocena wyników wskazuje, że obserwowane zmiany wskaźnika szybkości płynięcia badanych próbek są najprawdopodobniej efektem pożądanego szczepienia modyfikatora. Wniosek ten mogą potwierdzić wyniki oznaczań *MFR* próbek niezawierających inicjatora, w przypadku których po drugim etapie wytłaczania zaobserwowaliśmy pewien wzrost wartości *MFR* w stosunku do wartości charakteryzującej wyjściowy polietylen wynoszącej 7,97 g/10 min (rys. 7). Na częściową termooksydacyjną degradację tworzywa wskazują też rezultaty oznaczań ciężarów cząsteczkowych badanych polimerów (tabela 3).

Tabela 3. Wpływ ilości modyfikatora i DCP na wartość $\overline{M}_w$ PE-LD modyfikowanego dwuetapowo

Table 3. Effect of the modifier and DCP quantities on $\overline{M}_w$ of two-step modified PE-LD samples

Stężenie KI, % mas.	Stężenie DCP, % mas.	$\overline{M}_w$
0	0	82 734
5	0	75 469
5	0,3	48 097
5	1,1	44 544
8	0	66 797
8	0,3	43 116
8	1,1	38 975

Określiliśmy wreszcie wpływ omawianej metody modyfikacji PE na jego właściwości mechaniczne. Tabela 2 zawiera zestawienie uzyskanych wyników. Ze wzrostem stężenia KI w kompozycjach następuje stopniowe zmniejszenie ich naprężenia zrywającego. Należy jednak podkreślić, że dopiero gdy zawartość modyfikatora wynosi 10% mas. mechaniczne właściwości przy rozciąganiu kompozycji ulegają znacznemu pogorszeniu w porównaniu z właściwościami wyjściowego PE-LD, co zgodnie z przyjętymi ogólnie zasadami dyskwalifikuje otrzymane tworzywo pod względem zastosowania do celów praktycznych.

PODSUMOWANIE

W celu wprowadzenia do PE-LD grup funkcyjnych o działaniu hydrofilizującym z powodzeniem przeprowadzono szczepienie tego polimeru kwasem itakonowym wobec nadtlenku dikumylu jako inicjatora. Stwierdzono, że w zastosowanych warunkach modyfikacji na drodze dwuetapowego procesu wytłaczania w wytłaczarce dwuślimakowej nie następowało sieciowanie polimeru ani rozkład KI. Wykazano, że ilość modyfikującego KI nie powinna przekroczyć 8% mas., ponieważ większa jego ilość pogarsza właściwości mechaniczne tworzywa. Ze względu na efektywność procesu szczepienia korzystne jest na ogół stosowanie inicjatora w stężeniu 0,3—1,1% mas., a jedynie w kompozycjach o najmniejszej badanej zawartości KI (3% mas.) stężenie to powinno być mniejsze ze względu na niebezpieczeństwo równoczesnego usieciowania polimeru (duży udział w kompozycji inicjatora niewykorzystanego w procesie szczepienia KI). Celem dalszych naszych prac będzie zbadanie wpływu opisanej modyfikacji na szybkość rozkładu PE-LD w warunkach środowiska naturalnego.

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primarily determine the features associated with the conditions 3—5. For example, an additional third block soluble in the remaining blocks performs a role of a plasticizer of the intermediate phase (reduces the glass transition temperature T_g of this phase), the compatibilizer of the system components and the structure stabilizer. Thereby enables the preparation of the typical thermoplastic elastomers with very good parameters of high elasticity.

In this paper we want to indicate how a small modification of the chemical structure of only one of the blocks can influence on the thermal properties and structure of the multiblock terpolymers. Thereby, we will try to prove that we deal with such fine dependences in the case of the ternary systems. For this purpose we will compare two series of the multiblock terpolymers evaluating their thermal properties primarily by differential scaning calorimetry (DSC) method. Based on these properties we will try to evaluate the difference in their structures.

EXPERIMENTAL

Materials

The following terpolymers were selected for such assumed studies:

Series I — poly(tetramethylene terephtalate-*block*-oxytetramethylene-*block*-laurolactam) [-(PBT-*b*-PTMO-*b*-PA12)$_n$-],

Series II — poly(tetramethylene terephtalate-*block*-oxytetramethylene-*block*-dodecanemethylene sebacamide) [-(PBT-*b*-PTMO-*b*-PA12,10)$_n$-].

Syntheses of the oligoamide PA12, PA12,10 blocks and terpolymer -(PBT-*b*-PTMO-*b*-PA12)$_n$-, as well as -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- were previously described in details [5, 6, 10—14].

The size of the oligoester block PBT (a given degree of polymerization amounted to $DP_{\text{PBT}} = x$ respectively 2, 4, 7 and 11) varied in both series, whereas the content and the molecular weight of oligoether block PTMO were constant in the compared systems. The difference between these systems was associated with a small change of the chemical structure of polyamide block. The PA12,10 block has 12 and 8 methylene groups between the amide groups whereas the PA12 block has 11 methylene groups between amide groups. Such a small difference in the chemical structure does not influence or has a negligible effect on a value of the solubility parameters of oligoamide blocks [15].

Methods

The microcalorimetric examinations were recorded using DSC-2 (Perkin-Elmer) apparatus. The samples were examined in a triple cycle (heating-cooling-heating) at the temperature range from –150°C to +200°C. Both the heating and cooling rates were 10°C · min^{-1}.

T_g, a change of the capacity heat (ΔC_p), crystallization temperature (T_c), crystallization heat (ΔH_c), heat of melting (ΔH_m), and the melting temperature (T_m) of both series of the elastomers were determined using DSC method. The tensile data were collected at room temperature using Instron TMM tensile tester. Measurements of tensile stress (σ_r) and elongation at break (ε_r) were carried out using elongation rate 200 mm · min^{-1}. During recovery after elongation (ε_{ps}) measurements the rate of strain was 100 mm · min^{-1}.

Hardness (H) measurements were performed using Shore D apparatus (Zwick, type 3100) according to the standard DIN 53505 (ISO 863, PN-80/C-04238).

The limiting viscosity number ([η]) of the poly(ether-*block*-ester-*block*-amide) terpolymers in *m*-kresol was determined using an Ubbelohde viscometer IIA at 30°C.

RESULTS AND DISCUSSION

T_g and T_m values of the respective phase in the heterogeneous systems (multiblock polymers, polymer blends) may undergo the deviations from the values of T_g and T_m of the same phase occurring in the homogeneous material. These changes are caused by the factors, which disturb the phase structure. In the multiblock polymers composed of the amorphous soft phase and the hard crystalline phase, T_m depression of the crystalline phase is associated with mutual solubility of the blocks and with intermolecular and interfacial interaction. These factors also influence on T_g of the amorphous phase. Additionally, T_g is affected by stiffness of the block ends caused by the chemical bond (in macromolecule the blocks are chemically bonded and they do not have free chain ends).

The values of thermal transitions temperatures are shown in Figs. 1—4. The compositions and the basic properties of the terpolymers of both series are given in Tables 1 and 2 respectively.

Table 1. Composition of investigated -(PBT-*b*-PTMO-*b*-PA12)$_n$- and -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- terpolymers

Series	Sample	Composition (moles)			
		PTMO	PA12 or PA12,10	DMT	1,4-butanediol
I	1	2	1	3	5
	2	2	1	5	9
	3	2	1	8	15
	4	2	1	12	23
II	5	2	1	3	5
	6	2	1	5	9
	7	2	1	8	15
	8	2	1	12	23

T a b l e 2. **Basic properties of -(PBT-*b*-PTMO-*b*-PA12)$_n$- and -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- terpolymers (samples numbers according to Table 1)**

Series	Sample	[η], dL/g	H, Sh°D	σ_r, MPa	ε_r	$\varepsilon_{ps,100}$,%	ΔC_p, J/gK	T_g, °C	T_m, °C	DP_{PBT}
I	1	1.52	41	17.7	240	16	0.24	-67	146	2
	2	1.67	34	16.1	240	9	0.24	-63	135	4
	3	1.48	28	14.3	220	10	0.27	-57	126	7
	4	0.89	26	–	215	30	0.28	-54	108	11
II	5	0.80	42	11.5	199	15	0.09	-76	180	2
	6	1.01	54	17.9	176	34	0.04	-75	174	4
	7	1.14	40	15.0	200	16	0.15	-70	176	7
	8	1.01	41	12.5	180	17	0.17	-70	177	11

For the terpolymers -(PBT-*b*-PTMO-*b*-PA12)$_n$- of the I series (Figs. 1 and 2), a temperature range of the glass transition T_{g1} extends along with an increase in the molecular weight, DP_{PBT} of the ester block, whereas T_{g1} of the soft phase increases and the heat of crystallization of PTMO disappears, area under T_{m1} decreases. This relates to the deterioration of the phase separation of the whole system and "contamination" of the phase of PTMO blocks with other blocks. The endotherm (extreme) determining the heat of melting ΔH_m of the crystalline hard phase decreases and flatten along with an increase in DP_{PBT}. T_m decreases from 163°C for a pure block PA12 to 108°C for the terpolymer with the degree of polymerization $DP_{PBT} = 11$. Both these facts confirm that the crystalline phase decreased together with the deterioration of its perfections (excellence). In the copolymers -(PTMO-*b*-PA12)$_n$- the following phenomena were not observed: an increase in T_g of the phase composed of PTMO and the depression of T_m of the phase composed of PA12. Hence, it was assumed that PA12 blocks are insoluble in PTMO and the PTMO blocks are insoluble in PA12 [16]. Thus, the observed dependences in the described series of polymers are the results of the solubility of PBT (particularly the low molecular weight fractions) in PTMO and PA12.

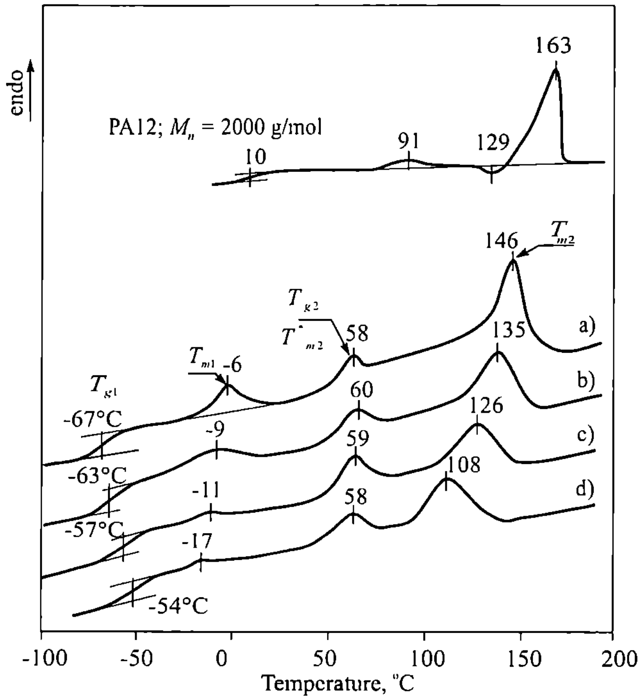

Fig. 1. DSC thermograms of -(PBT-b-PTMO-b-PA12)$_n$- terpolymers with variable values of DP_{PBT} [(a) = 2, (b) = 4, (c) = 7, (d) = 11] and constant molecular weight (PA12 = 2000 g/mol and PTMO = 1000 g/mol) subjected to heating (series I); T_{g1} — glass transition temperature of soft blocks; T_{m1} — melting temperature at low temperature region; T_{g2}, T^*_{m2} — glass transition and melting temperatures at middle temperature region; T_{m2} — melting temperatures of hard blocks

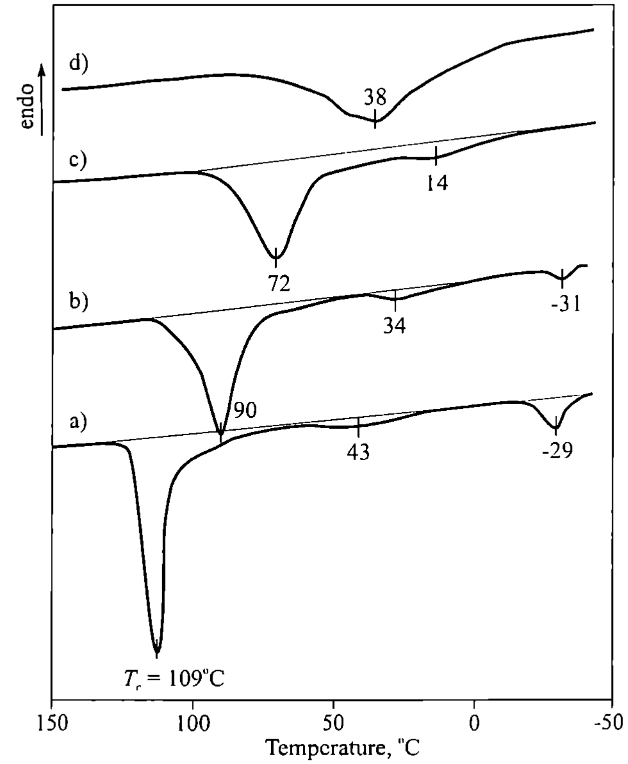

Fig. 2. DSC thermograms of -(PBT-b-PTMO-b-PA12)$_n$- terpolymers with variable values of DP_{PBT} and constant molecular weight subjected to cooling (series I); T_c — crystallization temperature of oligoamides blocks (for molecular weight of bloks, designations of curves and symbols see Fig. 1)

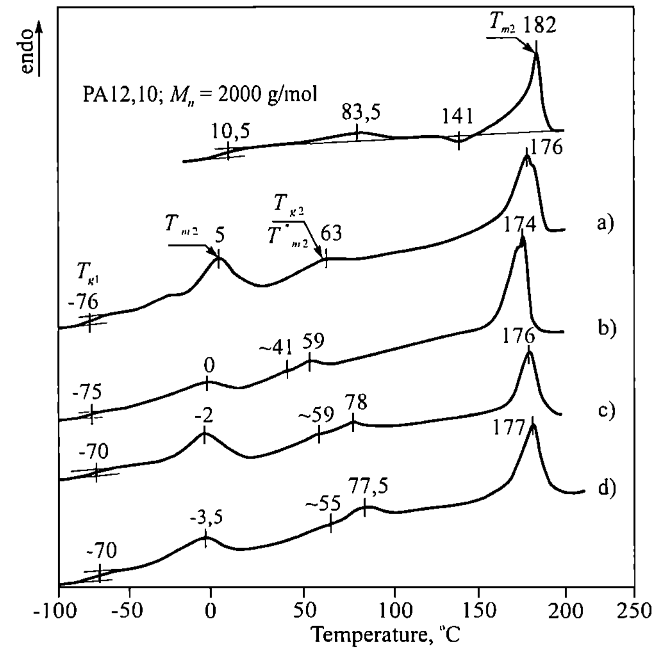

Fig. 3. DSC thermograms of -(PBT-b-PTMO-b-PA12.10)$_n$-terpolymers with variable values of DP$_{PBT}$ and constant molecular weight subjected to heating (series II); for molecular weight of blocks, designations of curves and symbols see Fig. 1

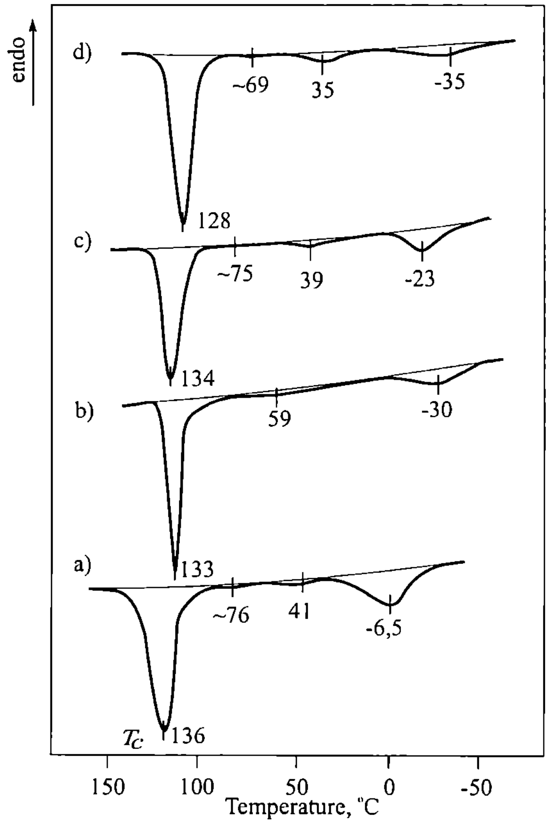

Fig. 4. DSC thermograms of -(PBT-b-PTMO-b-PA12,10)$_n$-terpolymers with variabe values of DP$_{PBT}$ and constant molecular weight subjected to cooling (series II); for molecular weight of blocks, designations of curves and symbols see Figs. 1 and 2

A slight decrease in T_g of the soft phase with an increase in DP_{PBT}, that is along with an increase in the contribution of the ester block, is characteristic for the second series of polymers (Figs. 3 and 4). If the soft phase was only composed of unbonded (free) PTMO blocks, its T_g should amount T_g = -89°C. Therefore, it is assumed, that stiffness of the chain ends causes an increase in T_g by about 10—15°C. Hence, the glass transition temperature of a pure phase of the PTMO blocks in terpolymers should be in the range –80—75°C. In the discussed group of terpolymers T_g is in the range from -70 to -76°C. This reveals that in the system -(PBT-*b*-PTMO-*b*--PA12,10)$_n$- the soft phase is one-component and has a homogeneous composition and there is a good separation of the soft phase and the hard one. A small fraction of PBT blocks in the soft phase occurs in terpolymers with a large content of PBT blocks in the system (DP_{PBT} = 7 and 11). The extreme of samples from series II, determining the heat of melting ΔH_m of the crystalline hard phase, does not change with an increase in DP_{PBT}. Melting temperature of pure PA12,10 block, which amounts 182°C, in the copolymers -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- fluctuates around 175°C. Such a small decrease is probably caused by the interfacial interactions in the system. This means that the crystalline phase did not undergo the deformation, thereby the PTMO and PBT are insoluble in PA12,10.

A parameter which characterizes the elastic properties is the recovery after elongation ε_{ps}. Good elastomers have $\varepsilon_{ps} \leq 10\%$ at elongation above 100%. This condition is fulfilled in the studied polymers by the samples of terpolymers -(PBT-*b*-PTMO-*b*-PA12)$_n$- (series I) with the number 2 and 3 for $DP_{PBT} < 7$ (Table 2). This allows to consider the terpolymers in which one of the block dissolves or is partly dissolved (low-molecular fractions) in the two remaining blocks as better elastomers than those with the components, which are mutually insoluble each in other.

CONCLUSIONS

The results presented in this paper allow to relate the structure and the properties of the three-component multiblock elastomers with the solubility of one component in the two remaining components of the system.

The terpolymers -(PBT-*b*-PTMO-*b*-PA12)$_n$- comprise the systems in which PBT component showing DP_{PBT} in the range 4—7 dissolves both in the phase of PA12 blocks (hard) and the phase of PTMO blocks (soft). Hence, in this system PBT block acts as a plasticizer, performs a role of a compatibilizer at the interphase (probably increases a fraction of the intermediate phase), and simultaneously acts as a stabilizer of the structure [5—7, 9]. Thereby, it enables the nanoseparation and shapes the nanostructure. Samples 1—3 of the series I are transparent.

The terpolymers -(PBT-*b*-PTMO-*b*-PA12,10)$_n$- show a slight solubility of PBT block in the flexible block phase and a lack of solubility in the phase of the hard block (PA12,10). Thereby in such three-component system, PBT block is stiffening (acts as a filler). A microseparation and a lack of nanostructures occur in these terpolymers. In the external appearance the terpolymers of this group (series II) are non-transparent.

So, for the investigated systems a small change in the chemical structure of the amide block significantly influences the structure, the phase separation and the properties of terpolymers.

The above conclusions confirm an argument that the block terpolymers show good elastic properties only in the case when one of the blocks partly dissolves in the phases formed from the remaining blocks.

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