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New multiblock terpoly(ester–ether–amide) thermoplastic elastomers with various chemical composition of ester block

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Abstract

New block terpolymers of the poly[oxytetramethylene-*block*-(multi-methylene terephthalate)-*block*-laurolactam] (aGT-b-PO4-b-PA12) with potential applications as elastomers have been obtained by melt polycondensation of dimethyl terephthalate or isophthalate (DMT, DMI), glycols (aG), poly(oxytetramethylene)diol (PO4, $M_w \approx 1000$ g mol^{-1}) and α,ω-dicarboxylic-oligolaurolactam (PA12 ≈ 2250 g mol^{-1}). The degree of polycondensation (DP) of poly(multi-methylene terephthalate) aGT amounts to $DP_{GT} = 4$. The influence of the number of carbons (a) separating the terephthalate groups as well as *meta* or *para* positions of the ester groups in the benzene ring of other blocks, on the synthesis, properties and structure of these elastomers have been evaluated. The influence of changes in chemical composition of ester block (GT) on the structure and thermal and mechanical properties of the terpolymers have been determined by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), wide-angle X-ray diffraction (WAXS) and other standard physical methods. The properties of aGT-b-PO4-b-PA12 depend upon the mutual interaction of PA12 blocks with PO4 blocks, whereas aGT with PO4 and aGT with PA12, respectively. The characteristic properties of the aGT-b-PO4-b-PA12 terpolymers is the large content of the interphase ($w_{iph} > 40\%$). The fraction of the interphase is dependent on the compatibility of aGT with PA12 blocks. The terpolymers prepared with the use of 3G and 4G exhibit the highest content of interphase. However, the 4GI-b-PO4-b-PA12 terpolymer has the highest degree of soft phase separation.

Keywords: Poly[ether-*block*-ester-*block*-amide]; Terpolymer block; Soft phase

1. Introduction

A part of multiblock copolymers of the $-(A_xB_y)_n-$ type which have the heterophase structure are classified to a group of thermoplastic elastomers (TPE). A macromolecule of the block elastomers consists of flexible and hard blocks distributed alternately. These blocks differ considerably in the physical and chemical properties. The flexible blocks are capable of formation of matrix (soft phase). The hard blocks, as a result of aggregation form the domains of these blocks, constituting the hard phase. Such heterophase systems are unique in that the dispersed domain structures are thermodynamically stable in the dispersed state. The phase separation in the block copolymers is restricted to molecular dimensions as a consequence of the incompatible block components being joined together, thus preventing gross physical separation of the two components as would occur with their simple mixtures [1–3]. In order to classify the block elastomers to TPE, their internal structure must comply the following conditions:

- the soft phase (responsible for the elastic properties) must possess a relatively small elasticity modulus and a relatively low glass transition temperature (T_g) and a small density. Hence, the chemical composition of blocks incorporated into the composition of this phase must assure weak intermolecular interactions, and a large capability for motion and rotation of the short sequences of chain (small cohesion energy); and
- the hard phase (responsible for the mechanical and processing properties) has to possess a relatively large modulus of elasticity, a high glass transition temperature (T_g) and melting temperature (T_m), and also a relatively high density. The blocks forming this phase have to characterise a tendency towards the aggregation with the same kind of segments. Thus, the strong intermolecular interactions occur, and so-called “pseudo cross-linking” reversible thermally, (van der Waals bonds, hydrogen

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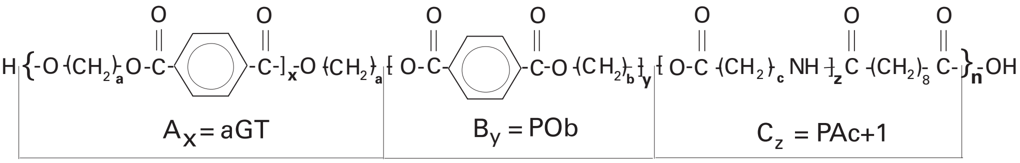


(I)

$A_x = aGT$ - oligoester block, a = 2 to 6, x = 4 (m.w.~ 880)
$B_y = POb$ - oligoether block, b = 4, y = 14 (m.w. ~1000)
$C_z = PAc+1$ - oligoamide block, c = 11 z = 11 (m.w. ~2250)

Scheme 1.

> bonds, ionic bonds, the ability to crystallisation, the polar and dispersive interactions). The intermolecular interactions of hard blocks affect the stabilisation of the phase structure of the entire polymeric system. The hard blocks have to be characterised by a considerably larger cohesive energy density of matter than the flexible blocks, thereby a higher thermodynamic potential. The potential difference comprises the driving force for the formation of a heterophase structure [1,3].

Therefore, important and a necessary feature of multiblock elastomers is a mutual thermodynamic incompatibility of blocks which depends upon both the chemical composition and the molecular weight. This feature determines the selection of blocks utilised for the manufacture of block TPEs. Summarising above, it can be concluded that the characteristic properties of block TPEs are a result of their specific molecular composition and the phase structure [4–6].

General characteristics of the block elastomers has been presented in a number of literature (reviews) surveys [7–9]. Taking into consideration the chemical composition, for a group of widely applied multiblock elastomers $(AB)_n$ have been classified [3,10,11]:

- copoly(ether–urethane)s, copoly(ester–urethane)s and copoly(ether–urethaneurea)s (PUE);
- copoly(ester–ether)s (PEE);
- copoly(ether–amide)s (PAE).

Numerous aspects of micro- and macrostructure of these elastomers have been elucidated in the last quarter of the century. The influence of the chemical and physical composition of the respective blocks on the relaxation properties, structural composition and on the microphase separation of the multiblock elastomers in copoly(ester–ether)s [12–26], polyurethanes [4,27–30] and copoly(ether–amide)s [2,31–35] have been investigated in detail. A model of the supermolecular structure which is distinctive of PUE and PAE has been proposed for PEE elastomers. PUE and PAE have a well-shaped amorphous phase, a large interphase and the pseudocrystalline or semicrystalline phase [2,5,23,27,30]. Whereas PEE elastomers possess the amorphous phase being a mixture of oligoether and short oligoester sequences, a small interphase and the spherulite crystalline phase relatively free from the lattice defects (crystal defects) [13–19,22].

From a hitherto own achievement in the field of PEE syntheses [36–40] and the research experience of the relaxation processes in the multiphase systems [41,42], out comes the idea of preparation of previously unknown poly(ester–ether–amide) block elastomer TPEEA, i.e. the terpolymer of the $-(A_xB_yC_z)_n-$ or $-[(B_yA_x)(B_yC_z)]_n-$ type. Predicting the occurrence of beneficial intermolecular interactions in such a ternary system, the possibility of preparation of a new type of polymers with the specific features was assumed by the composition of polyamide with polyether and polyester using the method of block melt condensation polymerisation. The system of the three blocks creates greater possibilities of controlling the desired (expected) features through the change of the quantitative composition or by preferential joining of segments. This also facilitates the synthesis process.

An initial point of TPEEA preparation was a typical synthesis of block PEE obtained from dimethyl terephthalate, 1,4-butanodiol and α,ω-oligo(oxytetramethylene)diol with the molecular weight 1000 g mol^{-1}, where dicarboxylic oligoamid is additionally introduced. Therefore, it can be assumed, that the synthesis of multiblock poly(ester–ether–amide) relies on a deep modification of PEE by dicarboxylic amide block [43–48].

In this paper I have described the synthesis of TPEEA and the relationship between the chemical composition of ester block and the properties in connection with the phase structure of TPEEA block elastomers.

The approximate chemical composition of the prepared terpolymer is represented by formula as shown in Scheme 1. I have prepared and studied these terpolymers, in which a in PE block is 2, 3, 4, 5, and 6, to determine the effect of lengthening the aliphatic component and of having odd and even numbers of carbon atoms in it. With $a = 4$, I have also prepared the PE block in the terpolymer with isophthalic acid, to study the effect of symmetrical and non-symmetrical substitution in the benzene ring. The following terpolymers were selected for the examinations:

- poly[(multi-methylene terephthalate)-*block*-(oxytetramethylene)-*block*-(laurolactam)] (aGT-*b*-PO4-*b*-PA12)
- poly[(tetramethylene isophthalate)-*block*-(oxytetramethylene)-*block*-(lauro-lactam)] (4GI-*b*-PO4-*b*-PA12).

2. Experimental

2.1. Materials

Synthesis of *a*GT-*b*-PO4-*b*-PA12 multiblock elastomers were carried out using the commercially available substrates, namely: dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), and ethylene glycol (2G)—Chemical Plant “Elana”; 1,3-propanediol (3G) 1,5-pentanediol (5G), and 1,6-hexanediol (6G)—Aldrich Chemie; 1,4-butanediol (4G)—BASF; α,ω-oligo(oxytetramethylene)diol (Terathane)—Du Pont with the number average molecular weight 1000 g mol^{-1}; dodecano-12-lactam (laurolactam), and sebacic acid—Aldrich Chemie. The lactam and the dicarboxylic acid are the substrates prepared in our laboratory: α,ω-dicarboxylic oligo(laurolactam) (PA12) with the number average molecular weight 2250 g mol^{-1} [43].

A catalyst, magnesium–titanate complex (Mg–Ti) prepared in our laboratory from tetrabutoxy titanate, was also utilised in the syntheses.

2.2. Synthesis

Synthesis of poly[ether-*block*–ester-*block*–amide] terpolymers with various chemical composition of ester block was a three-step process in the presence of magnesium–titanate organometalic complex as catalyst. The first step was the transesterification reaction of dimethyl terephthalate (DMT: 2 moles) and glycol (G: 3 moles). As a result GTGTG + $4CH_3OH\uparrow$ is formed. The second step, taking place simultaneously in another reactor, was the esterification reaction of α(ω-dicarboxylic-oligolaurolactam (PA12) with poly(oxytetramethylene)diol (PO4, PTMO). The obtained product is PO4-*b*-PA12-*b*-PO4 + $2H_2O\uparrow$. The third step was the polycondensation reaction of these two previously prepared intermediate compounds. GTGTG + PO4-*b*-PA12-*b*-PO4 → [PO4-*b*-PA12-*b*-PO4-*b*-$(GT)_x]_n$ + G$\uparrow$. Analysing the quantity of methanol and water collected from the reaction environment respectively, it was concluded, that the conversion in the transesterification reaction amounts to 98%, and the degree of esterification of this reaction 88%. The degree of conversion of esterification and transesterification reactions were expressed as a ratio of mass of released water or methanol to the stoichiometric amounts of these products, and reported as a percentage. A detailed description of this synthesis is given in previous papers [44–48]. The obtained products are light-cream coloured; they resemble PUE polyurethane elastomers by their appearance and on touch.

2.3. Sample preparation

Samples were obtained by injection moulding and by compression moulding. Injection moulding was carried out at ~50 MPa at a temperature approximately 20°C higher than the melting point (T_m) determined with a Boëthius apparatus. Compression moulding was performed at ~8 MPa at a temperature approximately 10°C higher than the melting point.

2.4. Determination

The relative viscosity η_{rel} of the α,ω-dicarboxylic oligoamides was determined by an Ubbelohde viscometer, according to PN 83/C-89039 (solvent H_2SO_4). The concentration of residual carboxylic end-groups [–COOH] was determined by means of titration analysis. A solution of oligoamide in a phenol–ethanol mixture was titrated by 0.02 N HCl in the presence of bromophenol blue until the colour changes to pink-violet. The concentration of amine groups [$-NH_2$] was determined by the titration of an oligoamide solution in benzyl alcohol with 0.02 N NaOH in the presence of phenolphthalein until the colour changes to pink.

The limiting viscosity number [η] of the poly[ether-*block*–ester-*block*–amide] terpolymers in phenol–trichloroethylene (50:50 vol/vol) was determined by an Ubbelohde viscometer II at 30°C. The melt flow index (MFI) of terpolymers was examined by a plastometer (CEAST type 6841) at 180°C. Optical melting points T_m were determined using a Boetius microscope (HMK type Franz Kustner Nacht KG) at a heating rate of 2°C/min. Hardness (*H*) measurements were performed on a Shore A and D apparatus (Zwick, type 3100) according to standard DIN 53505(ISO 868, PN-80/C-04238). The tensile data were collected at room temperature with an Instron TM-M tensile tester at a cross-head speed of 20 cm min^{-1}.

The microcalorimetric examinations were recorded on a DSC-2 (Perkin–Elmer) apparatus. The samples were examined in a triple cycle (heating–cooling–heating) in the temperature range from −120 to +200°C. The rate of both heating and cooling was 10°C min^{-1}. The glass transition temperature and melting temperature observed in the low-temperature region, T_{g1} and T_{m1} respectively, refer to the soft phase. The endotherms observed in the high-temperature region, T_{g2} and T_{m2}, refer to the hard phase.

The dynamic mechanical thermal analyses (DMTA) were performed on a Rheovibron DDV-II viscoelastometer in the temperature range from −120 to +200°C at 35 Hz. The storage modulus E', loss modulus E'', and loss tangent tan δ were determined.

WAXS experiments were carried out on a Rigaku goniometer and Ni-filtered CuK_α radiation from a Rigaku rotating anode generator. X-ray diffraction patterns were taken at room temperature.

Table 1
Properties of oligoamide

Symbol	η_{rel}[a]	[COOH] (μeq g^{-1}[b]	[NH$_2$] (μeq g^{-1}[c]	M_w (g mol^{-1})[d]	M_w (g mol^{-1})[e]	T_m (°C)[f]
PA12	1.101	893	8	2225	2250	172–178

[a] According to PN 83/C-89039.

[b] Solution of oligoamide in a phenol–ethanol mixture, titrated with 0.02 N HCl in the presence of bromophenol blue to change of color to pink-violet.

[c] Solution of oligoamide in benzyl alcohol in the presence of phenolphthalein, titrated with 0.02 N NaOH to change of color to pink.

[d] Calculated from the content of carboxylic groups.

[e] Calculated from the stoichiometric ratio of the substrates.

[f] Determined by means of the Boethius microscope, type HMK, heating rate 3° min^{-1}.

3. Results and discussion

Some properties of obtained α,ω-dicarboxylic-oligoamide PA12 are compiled in Table 1. A high content of carboxylic groups in these products attests to the reactivity of sebacic acid utilised for the regulation of the molecular weight. The differences between a value of the molecular weight enumerated from the amounts of the carboxylic groups and the viscometric testing, and this assumed theoretically, do not exceed 5% of measuring error, which implies to the correctness of the experimental assumptions. A value of the melting temperature of oligomer is lower than the temperature of respective polyamide, which is in agreement with the commonly known influence of the molecular weight of polymers on their melting temperature. Multiple syntheses of the dicarboxylic oligoamide PA12 were performed achieving the repeatability of results verified at a significance level of 99%.

3.1. Properties of PO4-b-GT-b-PO4-b-PA12

An increase in the limiting viscosity number values [η] determined during the synthesis was used as a measure of the polycondensation reaction progress. Fig. 1 illustrates the changes of [η] values during the polycondensation reaction in the synthesis of poly[ether-*block*–ester-*block*–amide] terpolymers, differing in the chemical structure of oligoester (GT) block. The terpolymers with 2GT block undergo the fastest polycondensation. The terpolymers with 4GT and 4GI blocks achieve the largest molecular weights. During the polycondensation of these three terpolymers, the highest power consumption by stirrer motor was observed.

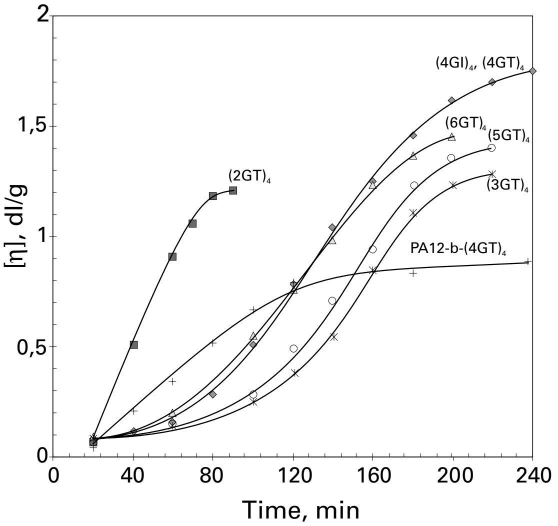


Fig. 1. The polycondensation reaction progress, expressed as an increase in [η] with time, for aGT-*b*-PO4-*b*-PA12 terpolymers (M_w block: PO4 = 1000, GT = 880, PA12 = 2250).

The aGT-*b*-PO4-*b*-PA12 terpolymers have good mechanical properties. The “stress–strain” curves of these terpolymers are characteristic for the thermoplastic elastomers (Fig. 2). The tensile strength values σ_r of the samples of terpolymers are satisfactory and similar to urethane elastomers (PUEs) with the same hardness. The elongation ϵ is smaller than for PUE.

The composition and preliminary characteristics of the terpolymers are given in Table 2. The number of carbons ***a*** separating the terephthalate groups in the ester block of *a*GT-*b*-PO4-*b*-PA12 terpolymers influences their limiting viscosity number, tensile data, T_m, MFI and elastic residue after 100% elongation. Hardness is the largest for the 2GT-*b*-PO4-*b*-PA12 terpolymer. The best mechanical properties have the terpolymers with the number $a = 2$ and 4, whereas the best elastic residues exhibit terpolymers with 3GT, 4GT, 4GI. The elastic residues are significantly better than that for PEE elastomers and comparable with PUE. The elongation ϵ is smaller than that for PUE. The terpolymers with 4GT

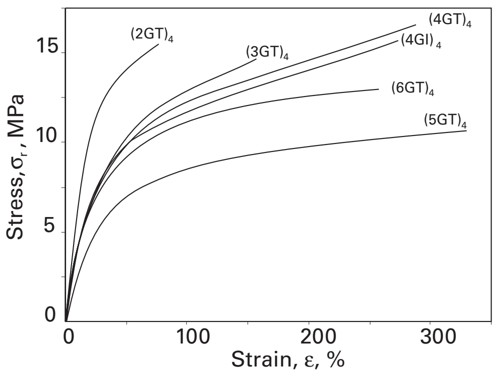


Fig. 2. The stress–strain curves of aGT-*b*-PO4-*b*-PA12 terpolymers at room temperature.

Table 2
The composition and the properties of *a*GT-*b*-PO4-*b*-PA12 terpolymers (DP, degree of polycondensation of ester block (GT); [η]-limiting viscosity number; MFI, melt flow index; *H*, hardness Shore A and D; σ_r, tensile strength; ϵ, elongation; T_m, melting point with Boethius apparatus; $\Delta l_{100} = [(l_k - l_p)/l_p]100\%$—residue after 100% elongation, where l_p is the initial length of sample, l_k the find length of sample after "elongation–recovery" cycle)

Polymer sample	PO4/PA12/DMT/BD-1,4 molar ratio	DP_{GT}	PO4/PA12/GT weight ratio (%)	[η] (dl g^{-1})	MFI (g min^{-10})	*H* (Shore A)	*H* (Shore D)	σ_r (Mpa)	ϵ (%)	Δl_{100} (%)	T_m (°C)
2GT	2/1/5/9	4	42/41/17	1.21	0.34	96	33	15.4	90	–	166–170.
3GT	2/1/5/9	4	42/41/17	1.44	1.22	91	28	14.9	160	10	138–146.
4GT	2/1/5/9	4	42/41/17	1.70	0.59	92	30	16.4	290	13	136–145.
5GT	2/1/5/9	4	42/41/17	1.38	1.04	91	28	12.3	330	18	140–148.
6GT	2/1/5/9	4	42/41/17	1.49	0.73	92	29	10.1	260	22	142–150.
4GI	2/1/5/9	4	42/41/17	1.64	0.65	92	29	15.8	270	14.5	135–146

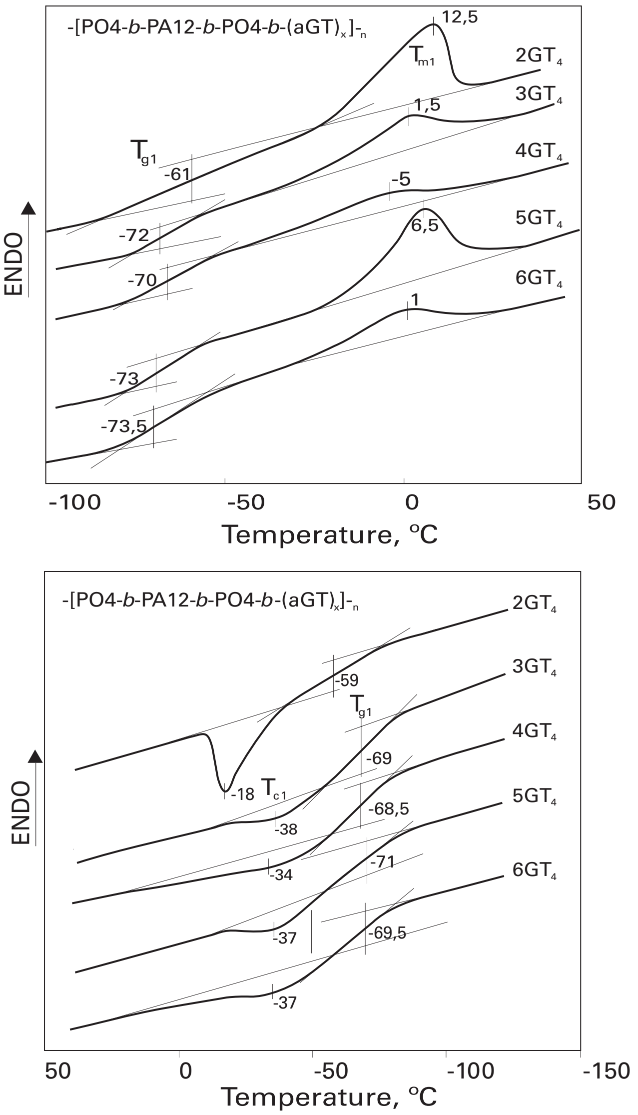


Fig. 3. The DSC thermograms of aGT-*b*-PO4-*b*-PA12 terpolymers in low-temperature region (heating, cooling).

and 4GI blocks exhibit the lowest melting points among the discussed set of the samples. Simultaneously, they are characterised by the smallest MFI, which attests about their highest viscosity in the molten state. This property was observed during the injection molding and compression molding of the samples. Their injection temperature was about 10°C higher than the other samples. In terpolymer with the number $a = 4$, the change of positions of the ester groups in the benzene rings from *para* into *meta* does not affect the mechanical and thermal properties of terpolymer.

3.2. Differential scanning calorimetry and dynamic mechanical thermal analysis

A suitable way of rapid investigation of the phase ratios is to combine DSC examination with DMTA. The results of

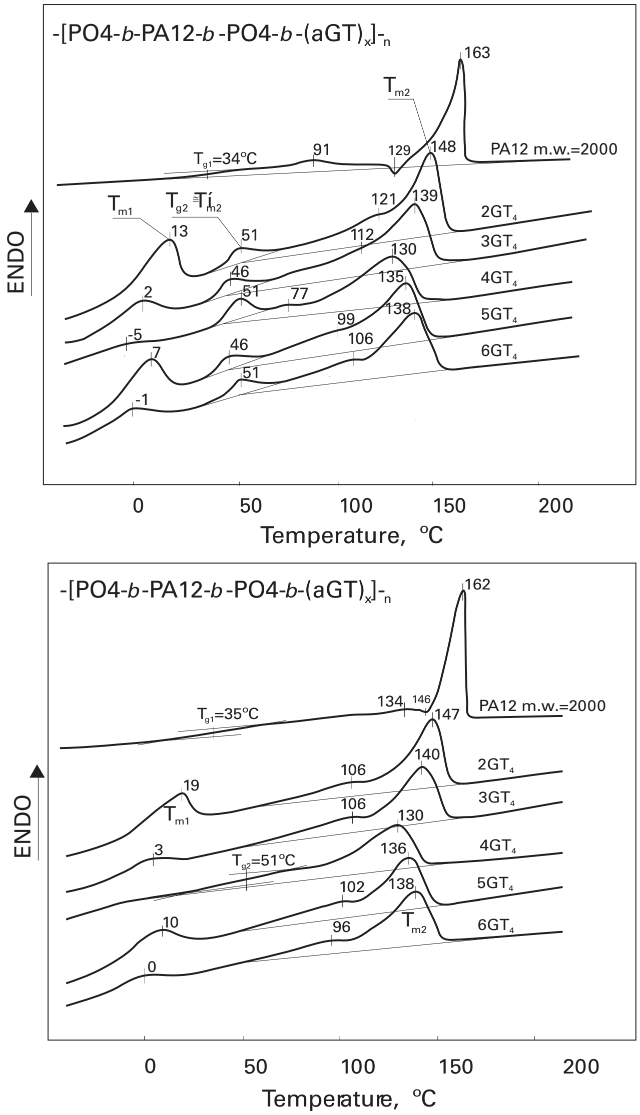


Fig. 4. The DSC thermograms of aGT-*b*-PO4-*b*-PA12 terpolymers in high-temperature region (first and second heating).

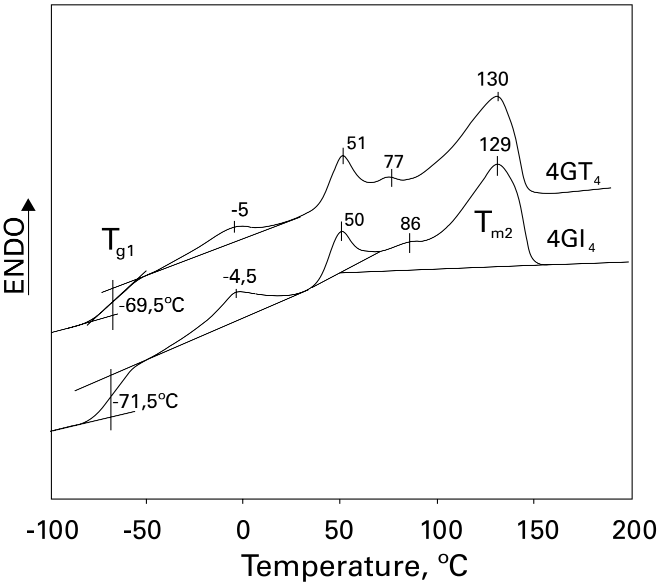


Fig. 5. The DSC thermograms of 4GT-*b*-PO4-*b*-PA12 and 4GI-*b*-PO4-*b*-PA12 terpolymers in low and high-temperature region.

DSC examinations of *a*GT-*b*-PO4-*b*-PA12 terpolymers are presented in Figs. 3–5. The samples of terpolymers were heated, cooled and reheated in the temperature range from -100 to $+250$°C. The glass transition temperature T_g, change of the specific heat ΔC_p, crystallisation temperature T_c, enthalpy of crystallisation ΔH_c, melting enthalpy ΔH_m, melting temperature T_m for the soft phase as well as the hard phase in a series of terpolymers, were determined. The values are compiled in Table 4. Additionally, the data of DSC analysis for the $(4GT)_4$, $PO4_{1000}$, $PA12_{2000}$ blocks and $(4GT)_4$-*b*-$PA12_{2000}$, $PO4_{1000}$-*b*-$PA12_{2000}$ and $PO4_{1000}$-*b*-$(4GT)_4$ *co*-blocks are cited in Tables 3 and 4 for the comparison purposes.

The constant value of the glass transition temperature ($T_{g1} \approx -70$°C) of a low-temperature region, is characteristic for *a*GT-*b*-PO4-*b*-PA12 terpolymers with number $a = 3$, 4, 5 and 6. This implies a good separation of the soft phase from the hard phase in the samples of terpolymers composed from the 3GT, 4GT, 5GT, 6GT and 4GI blocks.

A slight increase of T_{g1} in these terpolymers in relation to $T_{g,\ PO4} = -88$°C, allows to conclude that amorphous soft phase incorporated in the matrix composition is composed from the PO4 blocks and a small amount of the GT and PA12 blocks. The 2GT-*b*-PO4-*b*-PA12 terpolymer has a 10°C higher glass transition temperature than the other terpolymers. This indicates the increasing fraction of 2GT in the amorphous phase. Probably, the polydispersity index of the $-(2GT)_4-$ block formed during the polycondensation is larger than that of the remaining blocks (which is associated with the reactivity of glycols under the same reaction conditions). Therefore, in the polymer system of 2GT-*b*-PO4-*b*-PA12 occurs more shorter segments 2GT than in the remaining samples of examined series. The short sequences of 2GT are introduced in the PO4 amorphous phase as a result of segregation. The Hildebrand's solubility parameters for 2GT, 4GT, PO4 and PA12 amount to $\delta_{2GT} = 19.8/21.9\ J^{1/2}/cm^{3/2}$ [50]; $\delta_{4GT} = 21.6/23.15\ J^{1/2}/cm^{3/2}$; $\delta_{PO4} = 17/17.5\ J^{1/2}/cm^{3/2}$ [2,50]; $\delta_{PA12} = 22.1\ J^{1/2}/cm^{3/2}$ [2], respectively. From these parameters results, it is clear that the 2GT sequences are more readily soluble in PO4. This confirms the aforementioned conclusion. The 4GT block mixes well with PA12 $\delta_{4GT} = \delta_{PA12}$ and probably forms the system of a homogeneous mixture. A decrease of melting temperature of PA12-*b*-4GT significantly below T_m of pure blocks, suggests the formation of disordered crystalline structure and a spacious interphase. Thus, a hypothesis may be taken, that the 4GT block plasticise the polyamide hard phase [34]. The phenomenon of plasticisation of the hard phase also occurs in the 4GT-*b*-PO4-*b*-PA12 and 4GI-*b*-PO4-*b*-PA12 terpolymers. The total fraction of PA12 and

Table 3
The DSC study for three main blocks, and multi-blocks copolymers incorporated into the composition of terpolymers are prepared from them (T_{g1}, T_{c1}, T_{m1} = glass transition, crystallisation and melting point temperatures, respectively in low-temperature region; ΔC_{p1} = heat capacity change in T_{g1}; ΔC_{p2} = heat capacity change in T_{g2}; ΔH_{m1} = heat of melting at T_{m1}; ΔH_{c1} = crystallisation heat in T_{c1}; T_{g2}, T_{c2}, T_{m2} = glass transition, crystallisation and melting point tempeatures, respectively in high-temperature region; ΔH_{c2} = crystallisation heat in T_{c2}; ΔH_{m2} = heat of melting at T_{m2}; w_{cH}. (*degree of crystallinity determined by calorimetric method*) = ($\Delta H_t/\Delta H_{t,c}$); ΔH_t: melt entalphy of polymer sample = ΔH_{m2} or ΔH_{m1}; $\Delta H_{t,c}$-melt entalphy of completely crystalline polymer; $\Delta H_{t,c4GT}$ = 145 [49]; $\Delta H_{t,cPO4}$ = 172 [50]; $\Delta H_{t,cPA12}$ = 96 J g^{-1} [2])

Polymer sample	T_{g1} (°C)	ΔC_{p1} (J g^{-1} dag^{-1})	T_{c1} (°C)	ΔH_{c1} (J g^{-1})	T_{m1} (°C)	ΔH_{m1} (J g^{-1})	w_{cH} (%)	T_{g2} (°C)	ΔC_{p2} (J g^{-1} dag^{-1})	T_{c2} (°C)	ΔH_{c2} (J g^{-1})	T_{m2} (°C)	ΔH_{m2} (J g^{-1})	w_{cH} (%)
$PO4_{1000}$	− 88	0.64	2	91.3	19	111	64.5							
− $(4GT)_{4-}$	–	–	–	–	–	–		60	0.18	127	83.9	149–193	90.5	63.0
$PA12_{2000}$	–	–	–	–	–	–		10	0.17	134	75.6	134–169	81.0	84.5
$PA12_{2000}$-b-$(4GT)_4$	–	–	–	–	–	–		16	0.18	94	38	129–135	45.0	67
PA_{2000}-b-$PO4_{1000}$	− 77	0.09	− 3.5	23.5	20	21	37[a]	–	–	134	37	137–163	39.5	61[b]
$PO4_{1000} - b - (4GT)_4^7$	− 67	0.21	–	–	–	–	–	46	–	158	26	156–181	26.5	42.5[b]

[a] Soft phase.

[b] Hard phase.

Table 4
The DSC study results for aGT-b-PO4-b-PA12 terpolymers (T_{g1}, T_{c1}, T_{m1} = glass transition, crystallisation and melting point temperatures, respectively in low-temperature region; ΔC_{pl} = heat capacity change in T_{g1}; ΔH_{m1} = heat of melting at T_{m1}; ΔH_{cl} = crystallisation heat in T_{c1}; T_{g2}, T_{c2}, T^*_{c2}, T'_{m2}, T_{m2} = glass transition, crystallisation and melting point temperatures, respectively in high-temperature region; ΔH_{c2}, ΔH^*_{c2} = crystallisation heat in T_{c2}, T^*_{c2}; ΔH_{m2} = heat of melting at T_{m2}; and ΔH_2 = heat of melting at T'_{m2})

Polymer sample	T_{g1} (°C)	ΔC_{p1} (J g^{-1} dag^{-1})	T_{cl} (°C)	ΔH_{c1} (J g^{-1})	T_{m1} (°C)	ΔH_{m1} (J g^{-1})	$T'_{m2}T_{g2}$ (°C)	ΔH_2 (J g^{-1})	T^*_{c2} (°C)	T_{c2} (°C)	ΔH^*_{c2} (J g^{-1})	ΔH_{c2} (J g^{-1})	T_{m2} (°C)	ΔH_{m2} (J g^{-1})	T_{m2}–T_{g1} (°C)
2GT	− 61	0.26	− 18	6.6	13	11.0	51	3.3	45	110	1.7	28.2	106–147	31.7	209
3GT	− 72	0.16	− 38	2.5	2	4.9	46	3.0	24	106	2.0	26.5	106–140	29.6	211
4GT	− 70	0.20	− 34	4.2	− 5	1.4	51	3.7	30	94	2.5	21.2	130	25.6	200
5GT	− 73	0.19	− 37	2.6	7	9.7	46	2.9	23	103	2.0	26.2	102–136	28.6	208
6GT	− 73.5	0.23	− 37	5.3	− 1	5.0	51	3.0	35	96	2.2	25.0	96–138	27.3	211.5
4GI	− 71.5	0.24	− 35	4.3	− 4.5	3.9	50	3.5	20	94	1.7	23.1	86–129	24.8	200.5

Table 5
The DSC study results for aGT-b-PO4-b-Pa12 terpolymers ($\Delta C_{p,PO4} = 0.72$ J g^{-1} dag^{-1} = heat capacity change in T_g PO4 completely amorphous [2]; $\Delta H_{t,c}$ = melt entalphy of completely crystalline polymer, $\Delta H_{t,cPO4} = 172$; $\Delta H_{t,c2GT} = 140$ [50]; $\Delta H_{t,c4GT} = 145$ [49]; $\Delta H_{t,c6GT} = 143$ [49]; $\Delta H_{t,c4GI} = 192$ [49]; $\Delta H_{t,cPA12} = 96$ J g^{-1} [2]; w_s = fraction of soft block PO4 in terpolymer = 0.42; $w_h = (w_{PA12} + w_{GT})$ sum of fractions of hard blocks PA12 and GT = 0.41 + 0.17 = 0.58; SR$_s$ = degree of soft phase separation; $w_{cH,min} = (\Delta H_{m2}/w_h \Delta H_{t,cGT})$, $w_{cHmax} = (\Delta H_{m2}/w_h \Delta H_{t,cPA12})$, minimal and maximal degree of crystallinity of high-temperature region; $w_{iph} = (1 - \mathrm{SR}_s)w_s + (1 - w_{cHmax})w_h$, fraction of interphase; and the other notations same as in Table 4)

Polymer sample	$\frac{\Delta C_{p1}}{w_s \Delta C_{p,PO4}}$	$\frac{\Delta H_{m1}}{w_s \Delta H_{t,cPO4}}$	SR$_s$ (%)	T_{gPO4}–T_{g1} (°C)	T_{c2}–T^*_{c2} (°C)	T_{mPA12}–T_{m2} (°C)	$w_{cH,min}$ (%)	w_{cHmax} (%)	w_{iph} (%)
2GT	86	15.2	101.2	27	65	21	39	57	–
3GT	53	6.8	59.3	16	82	30		53	44.4
4GT	66	2	68	18	64	39	30	46	44.8
5GT	63	13.4	76.4	15	80	34		51	38.3
6GT	76	6.9	82.9	14.5	61	31	33	49	37.0
4GI	79	5.4	84.4	16.5	74	40	22	44.5	38.7

4GT in these terpolymers amounts to 58%. This suggests the formation of a rigid polymer with a moderate elasticity. However, the data in Table 2 contradict with this suggestion. Comparing the whole series of terpolymers without 2GT-*b*-PO4-*b*-PA12, it may be concluded that they have the T_m values close to 4GT-*b*-PO4-*b*-PA12. This allows to put a thesis in relation to them concerning the plasticised action of the GT blocks on the hard phase. This implies that 3GT, 4GT, 5GT and 6GT with the average degree of polymerisation, DP = 4, have the similar solubility parameters, which is closed to PA12 with the molecular weight of 2000. The 2GT-*b*-PO4-*b*-PA12 terpolymer is the only non-transparent plastic, harder than the other terpolymers, and crystallised in a greater degree. The endothermic effect determining T'_{m2} is observed in all the examined samples during the first heating. This effect overlaps with the effect of the specific heat variation of the hard phase (T_g). After cooling down, it appears again only just after 1 h. This effect was observed for many polymers crystallised from the melt. It is admitted that this is responsible for melting of microcrystalline species between the boundary layers of the large crystallites. For the terpolymers with odd number of carbons *a* in the ester block, T'_{m2} is by 5°C lower than in the case of the other terpolymers. The disorder of the chain symmetry in the ester block does not affect the value of this temperature. The enthalpy of this effect achieves a constant value independent on the chemical composition of ester block after 18 h. This may imply about the formation of the constant amount of fine crystallites being a part of the crystalline structure of aggregates. The small endotherms occurring before the main endothermic effect, connected with melting of the crystalline structures, originate from the deformation of crystalline lattice. Their values are contained in the enthalpy of melting of the high-temperature region.

The difference in the chemical composition of ester block practically does not influence on the maximal temperature range of application in practice ($T_{m2} - T_{g1} \approx 200°\mathrm{C} \approx$ constant). During cooling of terpolymers, two exothermic effects in the high-temperature region were observed. Probably they correspond to: ΔH_{c2} for the formation of crystallites and disordered crystalline structures with GT and PA12, whereas ΔH^*_{c2} for the reorganisation of structure (inclusion of relatively short segments of GT into the poor ordered crystallites). Table 5 presents the evaluations of the degree of soft phase separation. For the three-component systems, the mutual influence of the particular components on the degree of their phase separation should be expected. The method reported by Xie and Camberlin [2]was used for the determination of the degree of phase separation SR$_s$. However, this method was successfully applied for block copoly(ether–amide)s, in the case of 2GT-*b*-PO4-*b*-PA12, does not give an ambiguous result. The calculated SR$_s$ of this terpolymer amounts to 101% (?), which is contradictory to its considerable increase of T_g in relation to the other terpolymers. This means that the heat effect of T_g of the polyester amorphous phase overlaps with the effect of amorphous transition of 2GT or/and PA12, (in the discussed terpolymers, the most probable is that the effects of transition of amorphous GT overlaps, because it has a relatively small molecular weight in relation to PA12). Good, or even very good separation of PO4 blocks implies their small contribution in the formation of interphase. The minimal and maximal degree of crystallinity (W_{cH}) of a high-temperature region was determined. The minimal degree of crystallinity of a high-temperature region was calculated with the assumption, that crystallites originate from the ester blocks, whereas a maximum degree from the amide blocks. The WAXS results quoted below for the discussed terpolymers confirm the occurrence in them, mainly (α and γ(crystalline structure of polyamide 12. Hence, the results of the maximum value W_{cH} seem to be more truthful. The degree of crystallinity was calculated in relation to the amount of fractions of the rigid blocks. This procedure is justified since the PA12 and GT blocks are mutually soluble. The performed calculations enable the evaluation of the magnitude of interphase. The interphase fraction $w_{iph} = (1 - \mathrm{SR}_s)w_s + (1 - w_{cHmax})w_h$ in the evaluated terpolymers amounts from ∼35 to ∼45% by weight per terpolymer. The interphase is composed of hard blocks in about 60–80%, whereas only 20–40% of soft blocks. Taking into account the aforementioned deductions, it may be assumed that these are the GT blocks.

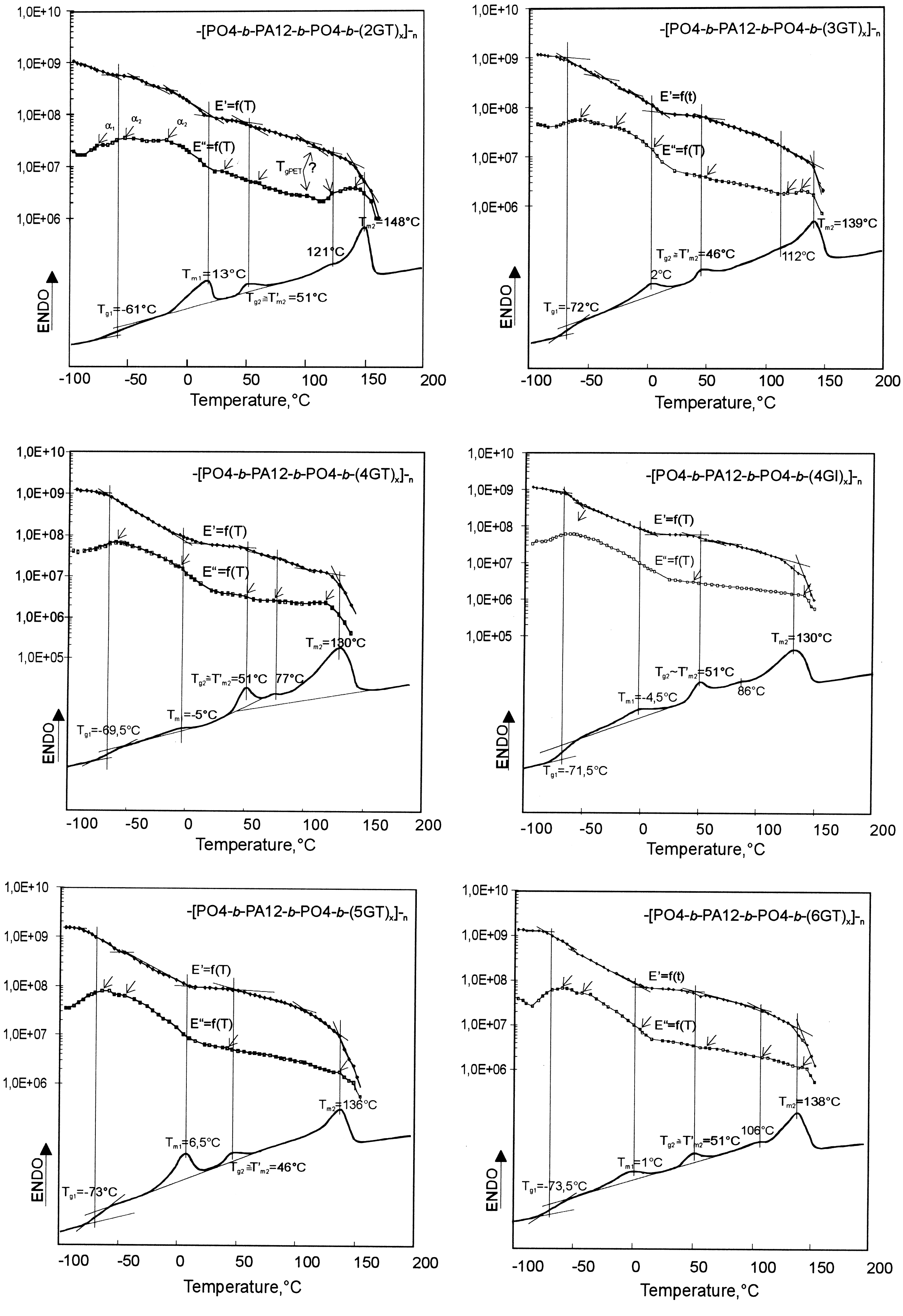


Fig. 6. The storage modulus (E'); the loss modulus (E'') and DSC thermograms of *a*GT-*b*-PO4-*b*-PA12 terpolymers vs. temperature.

The relaxation behaviour of all samples was studied by DMTA, measuring the storage modulus (E'), the loss modulus (E''), and the loss tangent (tan δ). The results of E' and E'' in comparison with the DSC are presented in Fig. 6 and tan δ in Fig. 7.

In the evaluated series of terpolymers, the storage modulus E' shows rapidly decreasing values near T_g and a wide “plateau” of elastic state. After that, a quick decrease of E' values near the melting temperature is observed. The width of a plateau of the elastic state practically determines the range of elastomer utilisations. The loss modulus shows a wide maximum E'' of relaxations of terpolymers that corresponds to the glass transition of the amorphous phase (relaxation α coupled with the large changes of modulus). The tan δ curves show (Fig. 7) damping peaks relevant to the amorphous phase. In the high-temperature region, the DMTA investigations completely overlap with the DSC results. The drops of modulus in the $E' = f(T)$ curves are observed, whereas in the $E'' = f(T)$ curves, the maxima of losses in the points determining the relaxation processes pertinent with T_{m1}, T_{g2}, T'_{m2} and T_{m2}. In the low-temperature region, the DMTA method appeared to be a finer method than DSC. Therefore, this method widen our knowledge about the amorphous phase and the interphase of GT-*b*-PO4-*b*-PA12 terpolymers. For the majority of examined samples, the $E'' = f(T)$ curves possess a broad relaxation peak α, composed of three smaller relaxation effects (relaxation transitions) $\alpha_{(}$, α_2, α_3. They may be linked with the glass transition temperatures for regions composed of pure PO4 and the mixture of PO4/GT and PO4/PA12 of the amorphous phase and interphase. The phenomenon of overlapping of three relaxation transitions is best seen in the peak α of 2GT-*b*-PO4-*b*-PA12 terpolymer ($SR_s > 100\%$ in this terpolymer confirms this fact). The distribution of relaxation α between the effects α_1, α_2 and α_3 disappear in the terpolymers with the ester blocks 4GT and 4GI. Thus, it can be assumed, that these blocks solubilise mainly in PA12 and only in a slight degree in PO4. The maxima of the damping values in the tan $\delta = f(T)$ curves have similar courses to the maxima of α relaxation of the $E'' = f(T)$ function. The terpolymers with 2GT, 3GT and 6GT blocks exhibit broad maxima of damping, and their shape is the result of overlapping of several relaxation transitions relevant to melting, and the glass transition of the amorphous phase and interphase. The shape of these maxima is influenced by dispersion in the amorphous phase of non-crystallisable blocks GT and PA12. The terpolymers with blocks 4GT, 4 GI and 5 GT exhibit narrower and higher damping peaks than the other terpolymers. Thus, the greater the miscibility of the GT blocks in PA12 and smaller in PO4, the higher and narrower are the peaks.

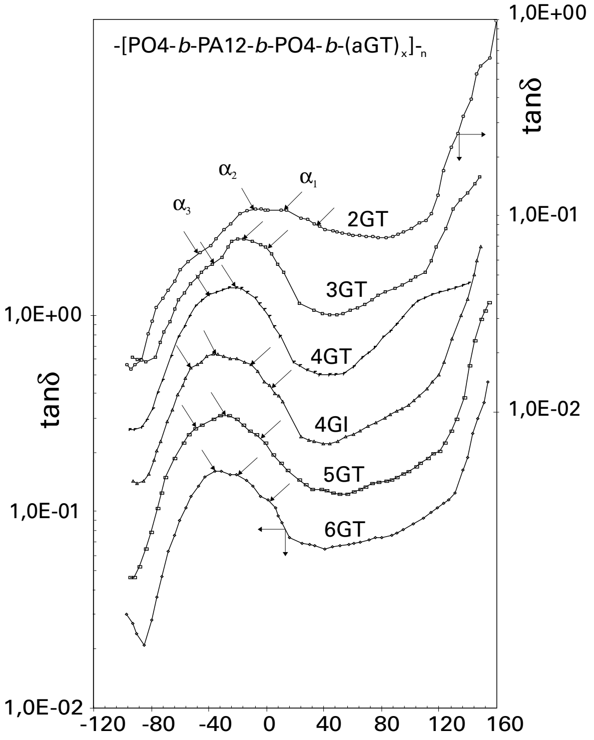


Fig. 7. The loss tangent (tan δ) of *a*GT-*b*-PO4-*b*-PA12 terpolymers vs. temperature.

The investigations of GT-*b*-PO4-*b*-PA12 terpolymers by WAXS method were performed in order to confirm their structure, previously determined by the DSC and DMTA methods. A quality assessment for the comparison of the diffraction patterns allows to conclude that a GT-*b*-PO4-*b*-PA12 exhibits pronouncedly outlined diffraction peaks of the polymorphic forms of the α and γ type corresponds to polyamide 12 (Fig. 8). This confirms a previous assumption that the crystalline phase of a high-temperature region is mainly composed of PA12.

In conclusion of these deductions, a general, demonstrative scheme of the structure of aGT-*b*-PO4-*b*-PA12 terpolymers

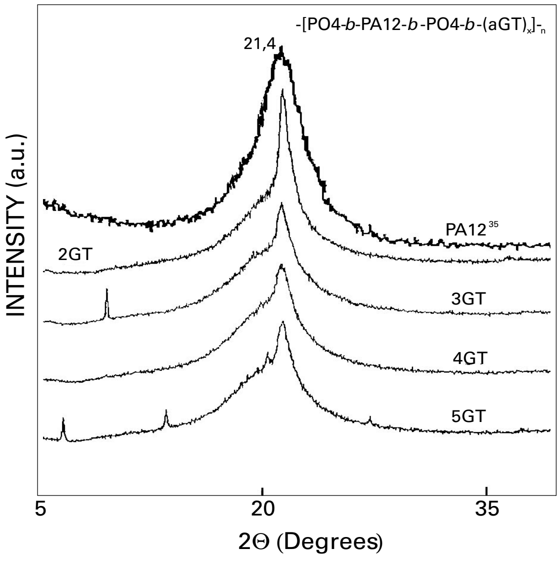
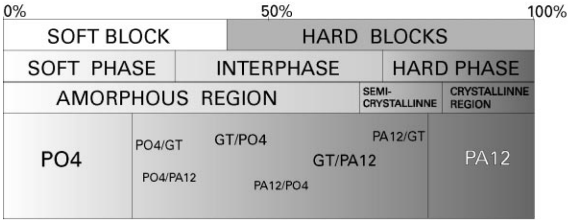


Fig. 8. The WARD patterns for *a*GT-*b*-PO4-*b*-PA12 terpolymers and PA12 homopolymer [35]. The PA12 homopolymer is rich in γ phase.

may be proposed. However, it should be emphasised, that this diagram is only a probable approximation of the internal composition of these terpolymers, since the quantity relationships in the systems PO4/GT, PO4/PA12 and GT/PA12 have not been determined.



The structure of the block polymers depends on the molecular weights of the respective blocks. The proposed scheme refers to poly[(multi-methylene terephthalate)-block-(oxytetramethylene)-block-(laurolactam)] terpolymers with the molecular weights of respective blocks: aGT ≈ 900; PO4 ≈ 1100; and PA12 ≈ 2200 g mol^{-1}.

4. Conclusion

A series of the new thermoplastic block terpolymers prepared by the polycondensation method in the molten state have been evaluated. It was found that they comprise a group of the thermoplastic elastomers. They are transparent products, with the exception of 2GT-*b*-PO4-*b*-PA12, which has a light-cream colour, and they have the mechanical properties similar to the PUE elastomers.

The change of the chemical composition of ester block GT with DP = 4, affects the mechanical and processing properties of these elastomers. It also influences on their structure through the effect of the phase separation and the interphase size.

The degree of phase separation of soft phase and the degree of crystallinity of hard phase was determined by the DSC analysis. The interphase size was also estimated, and the occurrence of the semicrystalline structures (disordered crystalline structure) was noticed. The DMTA method supplemented these data showing that the relaxation transition α, comprises the overlap of the substandard transitions originated from the homogeneous mixtures PO4/GT, PO4/PA12 and GT/PA12. A quality assessment of the WAXS diffraction patterns confirmed that the crystalline phase is composed of the diagram of the structure of terpolymers 2GT-*b*-PO4-*b*-PA12.

It has been concluded that the 3GT-*b*-PO4-*b*-PA12 and 4GT-*b*-PO4-*b*-PA12 terpolymers have the best elastic characteristics (residue after deformation). They also exhibit the largest interphase. This means that the interphase, so far underestimated, plays the role in the pseudocross-linking mechanism. From the technological point of view, it may be recognized that the block elastomers characterised by the increased fraction of the interphase (i.e. with block which are partially miscible), possess the properties similar to the soft rubbers, whereas the polymers with well-shaped phases (a residual interphase) similar to hard rubbers.

The functional, elastic and processing properties, technologically simple synthesis as well as the accessibility of the raw materials allow to conclude, that this type of block terpolymers may find applications in practice.

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