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Synthesis and Properties of Multiblock Terpoly(Ester-Aliphatic-Amide) and Terpoly(Ester-Ether-Amide) Thermoplastic Elastomers with Various Chemical Compositions of Ester Block

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Additional information is available at the end of the chapter

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Abstract

Two series of thermoplastic elastomers with various chemical compositions of ester block were prepared via the reaction of α,ω -dicarboxylic oligo(lauro lactam) (PA12, $M_w \approx 2000$ g/mol) with oligo(oxytetramethylene)diol (PTMO, $M_w \approx 1000$ g/mol) or linoleic alcohol dimer (DLAol) and with dimethyl terephthalate and a low molecular weight glycol (forming during the synthesis of the ester block). The degree of polycondensation (DP_{GT}) of poly(multi-methylene terephthalate) equals to $DP_{GT}=2$. The influence of the number of carbons separating the terephthalate groups, as well as the effect of *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. A nuclear magnetic resonance spectroscopy to carbon (^{13}C NMR) and Fourier transform infrared spectroscopy (FT-IR) were used to confirm their assumed chemical structure. The influence of chemical compositions of ester block on the functional properties and on the values of phase transition temperatures of the products have been determined. The thermal properties and the phase separation of obtained systems were defined by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), wide-angle x-ray diffraction (WAXS) and other standard physical methods. The mechanical and elastic properties of obtained polymers were evaluated.

Keywords: Poly(ester-ether-amide), poly(ester-aliphatic-amide), multiblock terpolymers, elastomers, phase structure

1. Introduction

A growing demand for polymeric materials in the packaging, sport, automotive, and medicine industries stimulates the search for innovative materials with thermal and mechanical properties individually tailored for a given field. Depending on the application, these materials have to be characterized, among others, by their resistance to chemical, mechanical, or biological factors. These requirements may be successfully satisfied by the thermoplastic multiblock elastomer (TPE).

They combine the end-use physical properties of vulcanized rubbers with the easy processing of thermoplastic [1–5]. The properties of TPEs are influenced by an appropriate phase structure and its thermal reproducibility in the heating-cooling cycle, functional qualities (large, reversible deformations) and the processing properties (possibility of multiple melting and solidifications). TPEs are considered as polymeric materials, in which, as a result of the phase separation, at least two phases (soft and hard) are distinguished, which must be thermodynamically immiscible to prevent the interpenetration. Hence, these are plastics possessing at least the two values of the physical transition temperatures, i.e., glass transition temperature T_g and melting point temperature T_m or T_{g1} and T_{g2} . These two temperatures determine the points at which the particular elastomer goes through transitions in its physical properties [6]. There are three distinct regions:

- at very low temperatures, below the T_g of the soft phase, in which both phases are hard, so the material is stiff and brittle;
- between the T_g of the soft phase and the T_m of the hard phase, in which material is soft and elastic, resembling a conventional vulcanized rubber. In these temperature range a modulus of elasticity stays relatively constant and this region is referred as “rubbery plateau” which is characteristic for TPEs;
- above the T_m of the hard phase, where the hard phase softens and melts and the material becomes a viscous fluid [7, 8].

Some of multiblock copolymers that have a heterophase internal structure are classified as the group of thermoplastic elastomers. Their macromolecule must contain two types of chain segments: amorphous, referred to as soft blocks, and hard blocks, which are mostly crystalline [9–12]. These blocks differ considerably in their physical and chemical properties. The soft blocks, which are capable of forming a soft-phase matrix, provides the elastomeric character, susceptibility to hydrolysis, and behavior of copolymer at low temperatures; while the hard segments determine processability, mechanical properties, hardness, and high temperature resistance. Hard segments are able to form intermolecular association with other hard blocks and these blocks form the domains of hard phase and are immersed in a soft-phase matrix. To classify the block elastomers to TPEs, their internal structure must comply with strict conditions. The soft phase should exhibit a relatively small elastic modulus, relatively low glass transition temperature, and a lower density. Moreover, these blocks should ensure weak intermolecular interactions and a large capability for motion and rotation of short sequences of chains. The hard phase must possess a relatively large elasticity modulus, high glass transition temperature or melting point, and high density. The segments that build this phase must

exhibit a tendency to aggregate with the same kind of segments. This aggregation leads to the thermally reversible “physical cross-linking”, which is stabilized by the van der Waals forces, high cohesive energy, hydrogen bonds, ionic bonds, the polar and dispersive interactions, or the ability to crystallization. The intermolecular interactions of rigid blocks affect the stabilization of the phase structure of the whole polymeric system. The hard segments must have a larger cohesive energy than the flexible segments and hence, a higher thermodynamic potential. The potential difference is a force that induces and stabilizes a heterophase structure [13–17].

The block copolymer will exhibit characteristics of a good elastomer if it complies with five inseparable conditions:

- macromolecules must be linear or weakly branched, which is responsible for thermoplasticity of these copolymer. Such macromolecules construction allows a close proximity of the hard blocks and intermolecular interactions;
- chemical composition of the blocks must have well-defined differences such that the thermodynamic condition of phase separation was fulfilled and the temperature spectrum of Young’s modulus had a wide plateau of elasticity;
- it must have appropriate phase composition depending on the type of blocks and their dimensions, which is responsible for the high elasticity features;
- it must possess an appropriate phase dispersion;
- it must have an appropriate interphase density, which is responsible for stabilization of the nanostructure.

The TPE properties are a result of the combination of the individual features of the respective blocks, hence a change of their chemical structure or their relative mass fraction, enables a modification of the macromolecule properties in the desired directions [18–25].

In the present chapter, the synthesis of multiblock thermoplastic elastomers and the relationship between the chemical structure of soft block and the properties in connection with the phase structure of terpolymers are described. The following terpolymers were selected for this research study:

- poly[(multi-methylene terephthalate)-block-(oxytetramethylene)-block-(laurolactam)]
xGT-PTMO-PA12
- poly[(multi-methylene terephthalate)-block-(linoleic alcohol dimer)-block-(laurolactam)]
xGT-DLAol-PA12

2. Experimental part

2.1. Materials

The following substrates were used: dimethyl terephthalate (DMT) - Chemical Plant “Elana”, ethylene glycol (2G), 1,3-propanediol (3G), 1,4-butanediol (4G), 1,5-pentanediol (5G), 1,6-

hexanediol (6G) - Sigma-Aldrich, poly(oxytetramethylene)diol with molecular weight 1000 g/mol (PTMO) - Du Pont, linoleic alcohol dimer (DLAol) - Croda, a titanate catalyst ($\text{TiO}_2/\text{SiO}_2$) - Sachtleben Chemic GmGH, thermal stabilizer (Irganox 1010) - Ciba Geigy, dodecano-12-lactam, sebacic acid - Aldrich Chemie. The lactam and the dicarboxylic acid are the substrates prepared in our laboratory: α,ω -dicarboxylic oligo(lauro lactam) (PA12) with the number average molecular weight 2000 g/mol [26, 27].

2.2. Synthesis of oligoamide blocks

The synthesis of oligoamides with molecular weight 2000 g/mol bi-ended with carboxylic groups was carried out.

Synthesis was carried out in a cylindrical shape with conical bottom 6-dm³ autoclave made of stainless steel. The ratio of height to reactor diameter is $h:d=3.5$. The heating system comprise a set of three resistance heaters enabling control of temperature in the range 20°C–400°C. The regulators are controlled by Fe-constantan thermocouples and Pt-100 thermoresistors.

A suitable amount of lauro lactam and sebacic acid, which was a stabilizer of molecular weight of the obtained oligoamides, was placed in the reactor. A small dose of water and phosphoric acid was added to simplify the initiation of the reaction. Before the synthesis, the autoclave was purged three times with nitrogen at the pressure of 0.5 MPa to gain an oxygen-free reaction environment. After that, the reaction mixture was kept in the reactor under a pressure of 0.1 MPa and then heated to a temperature of 300°C. A pressure would not exceed 1.6 MPa. The pressure was controlled by the removal of water vapor that contained a small amount of amide di- and trimers. This pressure stage of the reaction lasted 5 h. In the last half hour of this stage, the temperature raised to 305°C. Then, the pressure was reduced during 0.5 h to atmospheric pressure without decreasing the temperature. The pressureless stage (polycondensation) was carried out for 5 h under a flow of nitrogen. After the reaction was completed, the obtained oligoamide was extruded by compressed nitrogen into a tube with water that was vigorously stirring with bubbling air. To extract the residual by-products and unreacted lactam the finished product was rinsed three times with boiling water and then with distilled water. After drying in air and in a vacuum dryer at the temperature 60°C, the oligoamide was grounded and characterized.

2.3. Synthesis of multiblock thermoplastic elastomers

Synthesis of block terpolymers proceeded in the two stages. The first stage was the transesterification reaction of dimethyl terephthalate with glycol leading to the formation of polyester and the release of methanol and the esterification (in a separate reactor) of α,ω -dicarboxylic oligo(lauro lactam) with oligo(oxytetramethylene)diol or linoleic alcohol dimer (by-product is water) in the presence of catalyst. From the respective amounts of methanol and water, it was concluded that the conversion in the transesterification reaction was 95% and the degree of esterification was 90% (degrees was expressed as the weight ratios of the released methanol or water to the respective stoichiometric amounts of these products). The second stage of the process comprises the specific condensation polymerization of mixed intermediates obtained in the first stage of synthesis. The course and parameters of synthesis is presented in Figure 1.

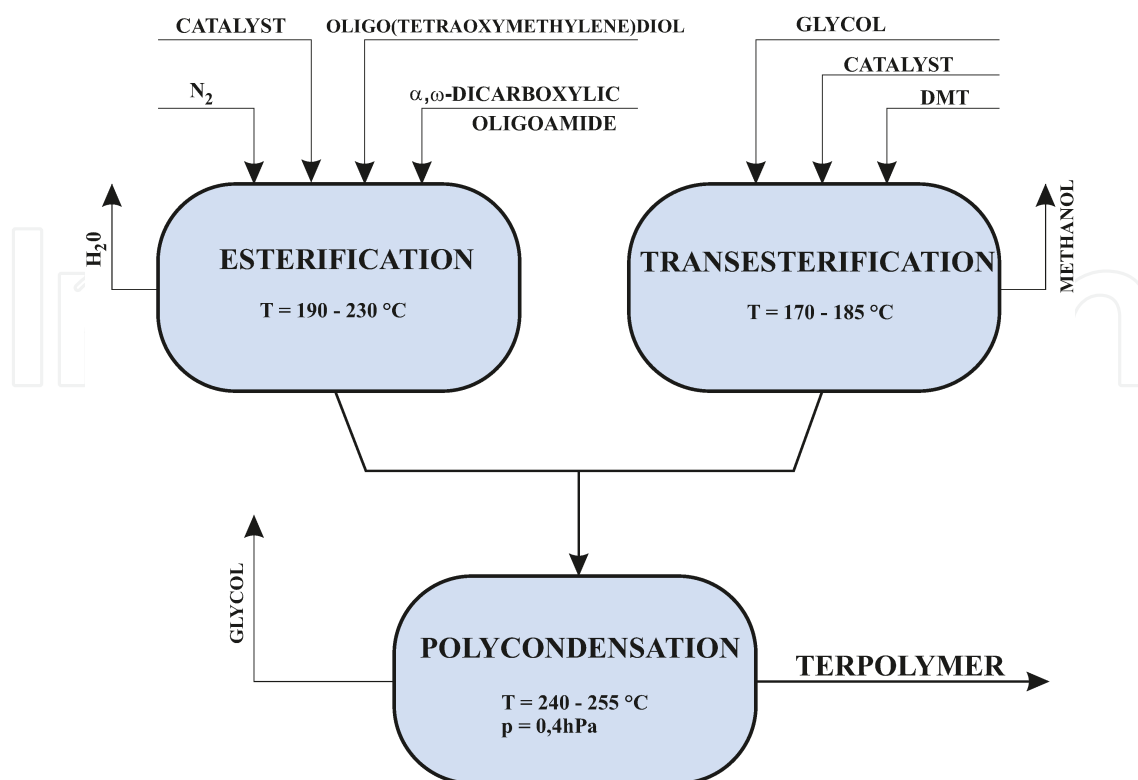


Figure 1. Structure flow chart.

Preparation of terpolymers relies on the replacement in the poly(multi-methylene terephthalate) macromolecule (xGT), a certain part of fragments originated from the terephthalic acid by the dicarboxylic oligoamide block, which was derived from glycol by the oligoetherdiol or alifatic block (Figure 2).

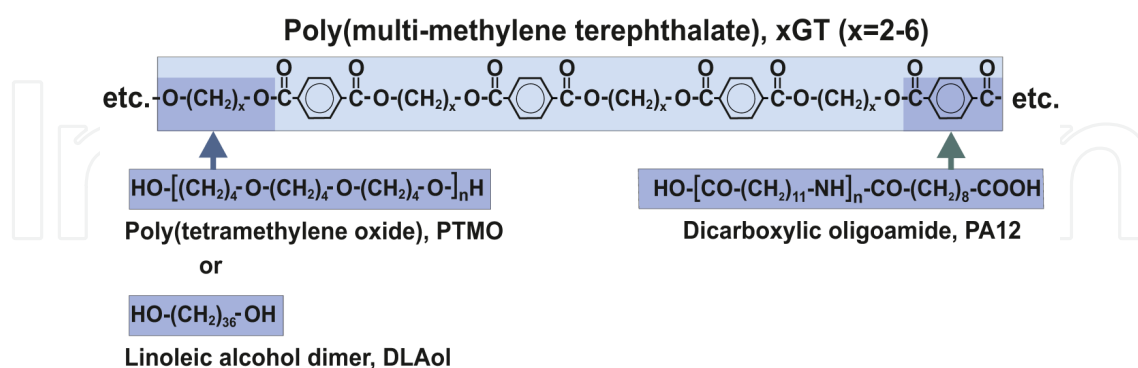


Figure 2. Multi-methylene terephthalate modification.

The previous investigations carried out by Ukielski [28–30] have demonstrated that the molar ratio of PTMO with molecular weight 1000 g/mole to PA12 with molecular weight 2000 g/mole should be ranged between 2 and 3.5. This determines a relatively small fraction of the xGT sequence in the soft phase, large degrees of separation of both soft and hard phase and

comparable fraction of the respective blocks in the interphase. Based on the results of previous works, the molar ratio of PTMO/PA12=3 was assumed for further studies. A two series of terpolymers composed of the blocks PTMO or DLAol and PA12 with the constant molar weight amounting to respectively, 1000 g/mole, 570 g/mole and 2000 g/mol and xGT block, with constant degree of polycondensation amounting $DP_{xGT}=2$, which is formed during the synthesis, were prepared. The series differ in a chemical structure of the ester block. The molar ratio and weight ratios of reagent used for the synthesis were presented in Table 1.

Sample	Glycol	Soft block	m_{soft}	m_{PA12}	m_{DMT}	m_{xG}	w_{PTMO}	w_{xGT}	w_{PA12}	Series
1	2G	PTMO	3	1	5	9	0,520	0,133	0,347	I
2	3G	PTMO	3	1	5	9	0,515	0,141	0,343	
3	4G	PTMO	3	1	5	9	0,510	0,150	0,340	
4	5G	PTMO	3	1	5	9	0,505	0,158	0,337	
5	6G	PTMO	3	1	5	9	0,501	0,166	0,334	
6	2G	DLAol	3	1	5	9	0,382	0,172	0,447	II
7	3G	DLAol	3	1	5	9	0,377	0,182	0,441	
8	4G	DLAol	3	1	5	9	0,373	0,192	0,436	
9	5G	DLAol	3	1	5	9	0,368	0,201	0,430	
10	6G	DLAol	3	1	5	9	0,364	0,211	0,425	

m – molar ratio, w – weight fraction

Table 1. The composition of terpolymers with constant molecular weights of PA12=2000 g/mole and PTMO=1000 g/mole; $DP_{xGT}=2$.

3. Results and discussion

3.1. Properties of α,ω -dicarboxylic oligoamides

Assumed molecular weight of the oligoamide was 2000 g/mole. The difference between the molecular weight values, calculated from the amounts of the carboxylic groups and the assumed theoretical values do not exceed 2.5% of the experimental error, which supports the correctness of the experimental assumptions. The melting temperature values of the PA12 oligoamides are lower than the melting temperature of the polyamide 12, which is 179°C.

Usage of sebacic acid as the molecular weight stabilizer leads to dicarboxylic oligoamids. Obtained oligoamids had coherent with assumed molecular weight values, didn't contain amid groups, and may be used as hard block in various types of thermoplastic multiblock elastomers. Some properties of the obtained α,ω -dicarboxylic oligoamides are presented in Table 2.

Sample	[-COOH], $\mu\text{eq/g}$	[-NH ₂], $\mu\text{eq/g}$	M _n , g/mole	T _m , °C
OA1	1013	4	1974	161-170
OA2	1004	2	1992	162-173
OA3	992	0	2016	167-173
OA4	1032	0	1938	157-167
OA5	1000	2	2000	160-171

[-COOH] – the concentration of carboxyl groups, [-NH₂] – the concentration of amino groups, M_n - average molecular weight, T_m – melting temperature range determined by means of the Boethius microscope

Table 2. Properties of obtained oligoamides.

3.2. Properties of TPE

The number of carbons x separating the terephthalate groups in the ester block of TPEs influences all their properties, which were presented in Table 3.

Sample	$[\eta]$, dL/g	H, Shore A	H, Shore D	p _{H₂O} , %	p _{benzene} , %	σ , MPa	E, MPa	ϵ , %	T _m ⁱ , °C	T _m ^f , °C
1	1,25	84	29	2	134	6,9	18,1	112	135	150
2	1,40	76	26	2	174	4,7	13,6	200	122	135
3	1,68	76	24	0	182	12,5	29	165	157	151
4	1,29	78	24	1	174	6,5	21,1	253	128	135
5	1,32	75	23	3	204	12,1	27	132	146	150
6	1,29	84	19	1	84	13,7	25,4	99	133	148
7	1,55	87	19	1	82	14,5	23,6	81	125	138
8	1,74	87	19	1	75	17,5	46,6	123	141	164
9	1,35	69	16	0	96	13,2	29,8	127	129	150
10	1,25	69	16	4	117	17,4	48,9	104	150	161

$[\eta]$ – limiting viscosity number, H – hardness, p_{H₂O} and p_{benzene} – absorbability of water and benzene, respectively, σ – tensile strength, E – the Young module, ϵ – elongation at break, T_mⁱ, T_m^e - initial and end of melting point

Table 3. The properties of terpolymer elastomers TPE with variable chemical structure of ester block.

TPEs have the satisfactory molecular weights and good mechanical properties when the values of their limiting viscosity numbers are larger than $[\eta] > 1.25$ dL/g. The $[\eta]$ values of obtained polymers have proved that they are composed of the macromolecules with satisfactory molecular weights. The ability to swell depends on the polarity of the solvent and the chemical structure of the polymer macromolecule. Swelling occurs only in the amorphous structural

zones of the terpolymer. It is therefore a measure of the quality and content of the continuous phase. As a physical phenomenon indicates an internal cross-linking of the polymer and describes its physical structure. Absorbability increases with increasing mobility of the macromolecules and decreases with an increase in cohesive energy between them. The obtained results of swelling in water indicate for a hydrophobic character of all the prepared polymers. The swelling does not exceed 4%, which indicates the water penetration in the amorphous phase of polymer only in a slight degree. An increase in the number of carbons separating the terephthalate groups in the ester block of TPEEAs causes an increase of absorbability of benzene and decrease of hardness, due to an increase in amorphous phase content. Flexible blocks create more and better polymer matrix and the content of crystalline phase decreases. It results in the relaxation of the structure and distance from other polymer macromolecules, thus easier benzene penetration into the material and less rigidity.

3.3. Chemical structure of TPEs

The FT-IR spectra [31, 32] of terpolymers selected from each series are shown in Figure 3 and 4. Obtained copolymers had all characteristic bands for esters, aliphates or ether, and amides, which are presented in Table 4.

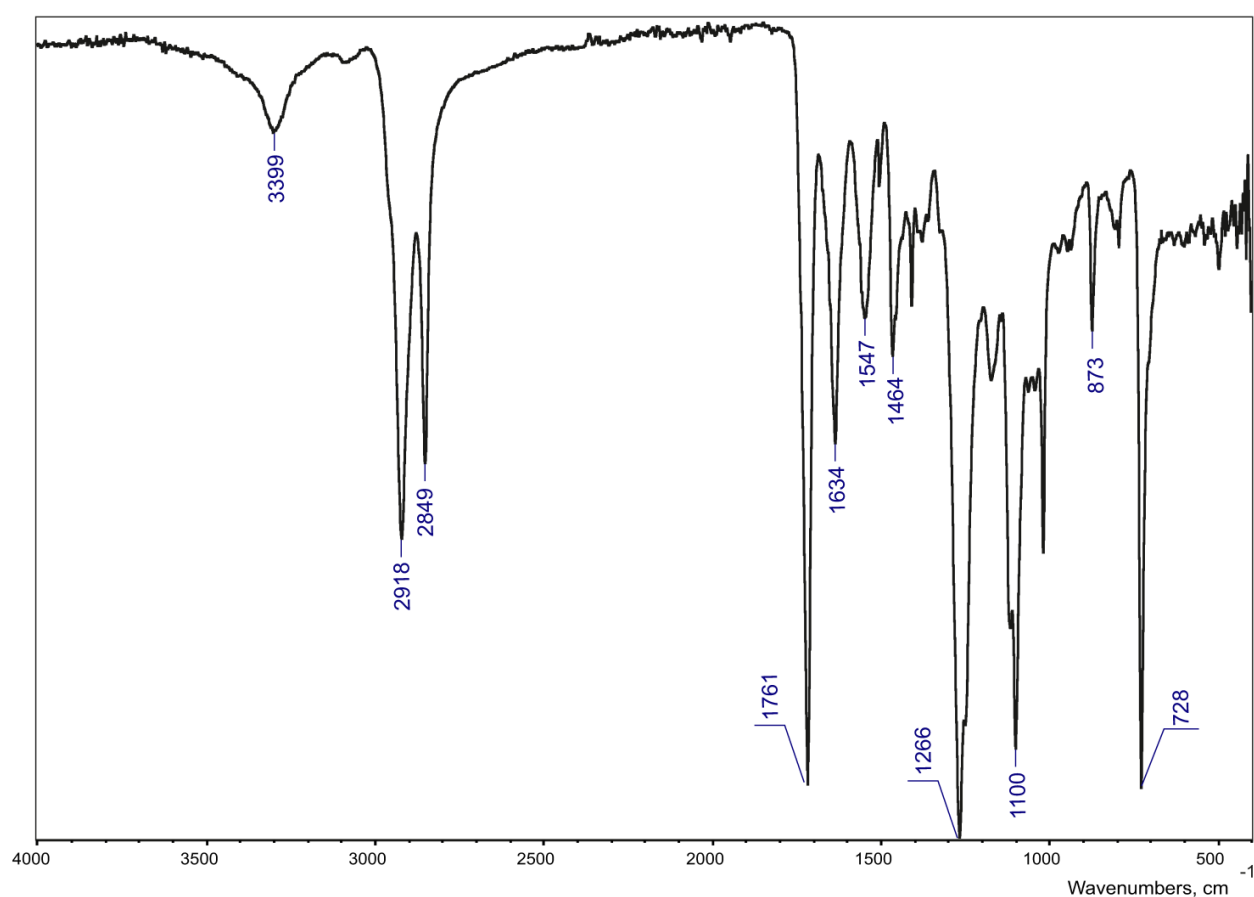


Figure 3. FT-IR spectra for terpolymer 3GT-DLAol-PA12.

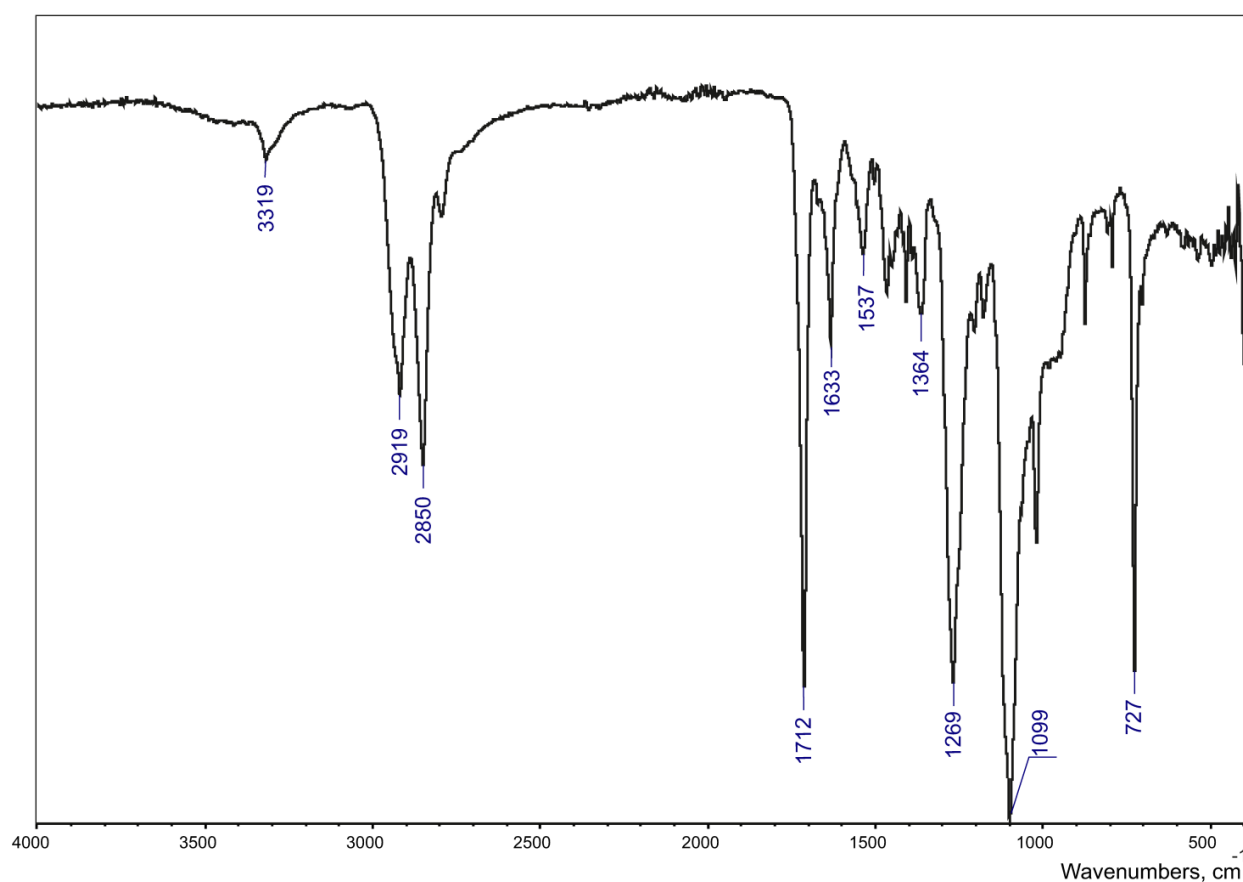


Figure 4. FT-IR spectra for terpolymer 3GT-PTMO-PA12.

3GT-PTMO-PA12 band frequency, ppm	3GT-DLAol-PA12 band frequency, ppm	Chemical structure
3319	3399	Hydrogen-bonded N-H stretching
2919 and 2850	2918 and 2849	CH ₂ asymmetric and symmetric stretching
1712	1761	Ester C=O stretching
1633	1634	Amide I, amide C=O stretching
1537	1547	Amide II, C-N stretching + amide C=O in plane bonding
1364	1371	CH bond, CH ₂ twisting
1269	1266	Amide III, C-N stretching + amide C=O in plane bonding
1099	1100	C-O-C asymmetric stretching
727	728	Aromatic C-H out of plane bonds

Table 4. Wavenumbers and assignments of FT-IR band exhibited by obtained terpolymers.

Chemical structure of new materials was also verified with ^{13}C NMR spectroscopy [31–34] and the results with peak assignments are presented in Figures 5 and 6. Analysis of the ^{13}C NMR spectra showed the presence of all characteristic groups present in the esters, ethers or fatty acids, and amides. Signals are noted in the range 26.89–218.53 ppm and their interpretation are detailed in Table 5.

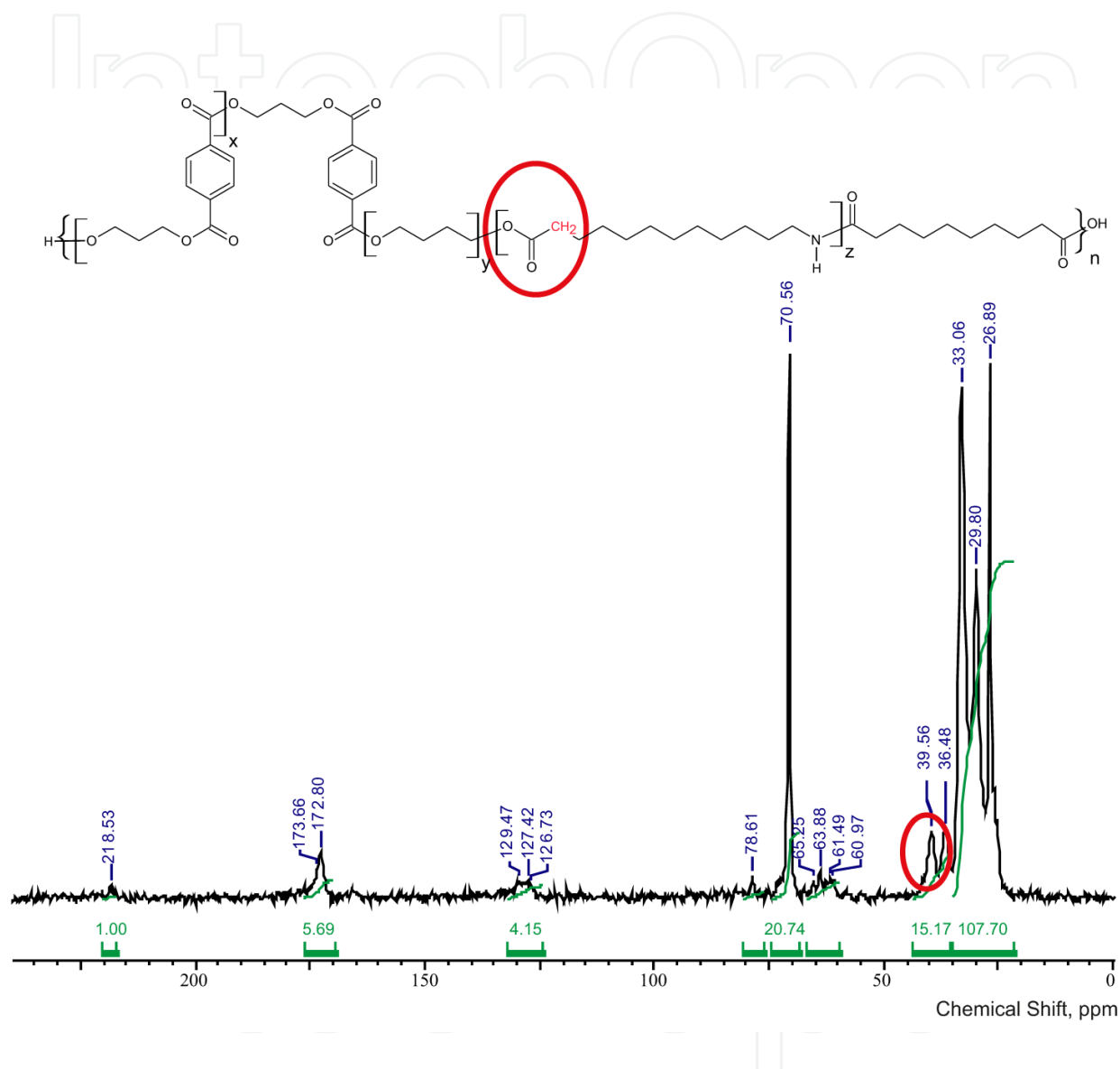


Figure 5. ^{13}C NMR spectra of terpolymer 3GT-PTMO-PA12.

On the ^{13}C NMR spectrum the peak presence at 39.56 ppm indicates that amide block is built into copolymer macromolecule.

^{13}C NMR and FT-IR analysis confirmed the assumed chemical structure of terpoly(ester-ether-amides) and terpoly(ester-aliphatic-amides). However, one should bear in mind that the terpoly(ester-ether-amide)s and terpoly(ester-aliphatic-amide)s are random block polymers.

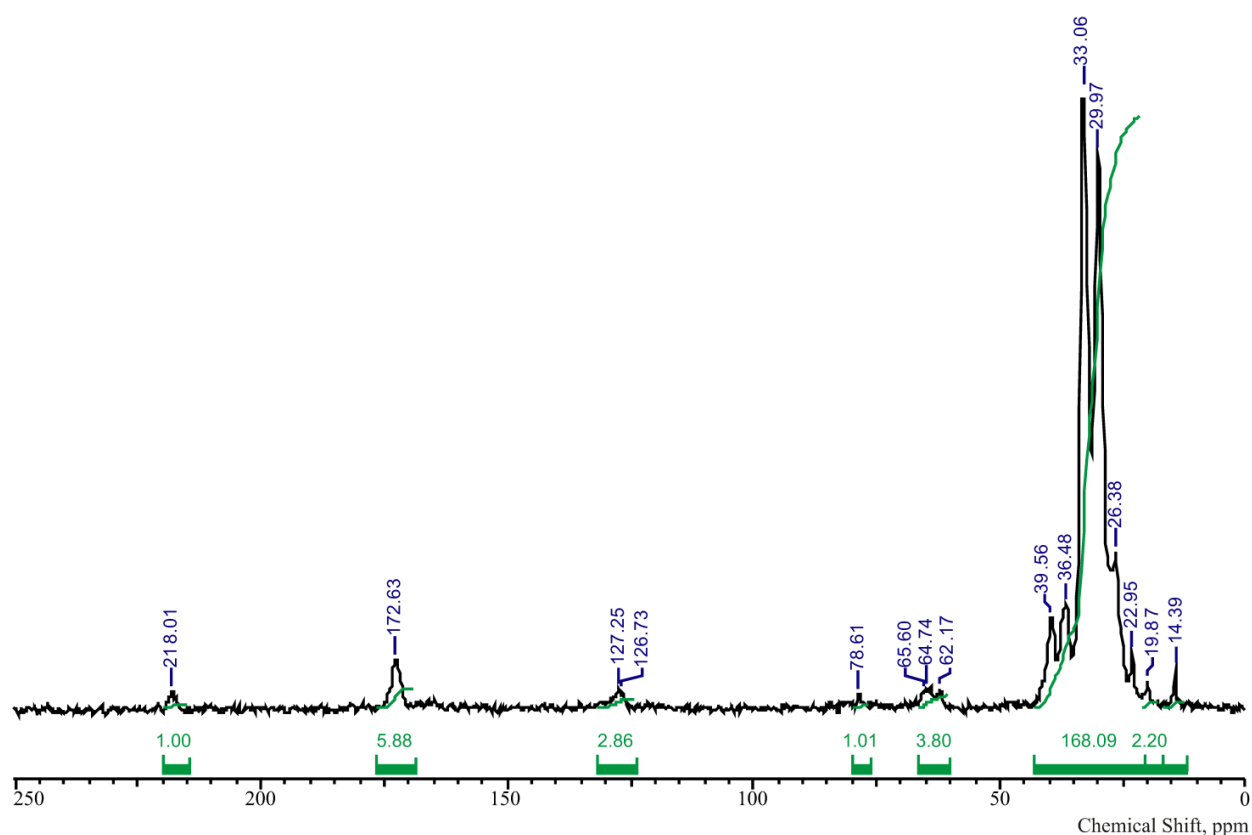


Figure 6. ^{13}C NMR spectra of terpolymer 3GT-DLAol-PA12.

Band frequency, Chemical structure ppm	
218.5	C atoms of the amide group
172-173	C atoms of the carbonyl group
126-129	C atoms in the aromatic ring
70.6	C atoms in the ether group
61-65	CH_2 groups linked to the carbonyl group through an oxygen atom
39.6	CH_2 groups bonded to a carbonyl group
36.5	CH_2 groups bonded to the C atom of the amide group
33	All other CH_2 groups in the oligoamide chain
29.8	CH_2 groups of β fragments bonded to amide or carbonyl groups or CH_2 groups of β fragments of glycol
26.9	Polyether CH_2 groups bonded to the other CH_2 groups
19 - 26	C atoms in the aliphatic chain
14.39	C18 atoms in the aliphatic chain

Table 5. Chemical shifts (ppm) of terpoly(ester-ether-amides) and terpoly(ester-aliphatic-amides).

3.4. Mechanical properties

The ability of instant recovery after the deformation is expressed by the elastic elongation (ϵ_s) and the area A, which is proportional to the dissipated elastic energy. It is a measure of the quality of the spatial network of the elastomer. High elastic elongation (ϵ_{hs}) and the area B, which is proportional to the dissipated energy, characterize the ability of a material to have delayed recovery after deformation. It is a measure of the quality of the continuous phase capable of viscoelastic response. Permanent set (ϵ_{ps}) corresponds to the irreversible changes that have occurred in the material under the stress, most likely related to the change in the spatial distribution of domains. The area C is proportional to the accumulated energy. Received two types of mechanical hysteresis loops. The first type was obtained by stretching a terpolymer sample from 10% to 100% at elongation growing by 10% (Figure 7). The second one was obtained by stretching at constant elongation of 100% (Figure 8).

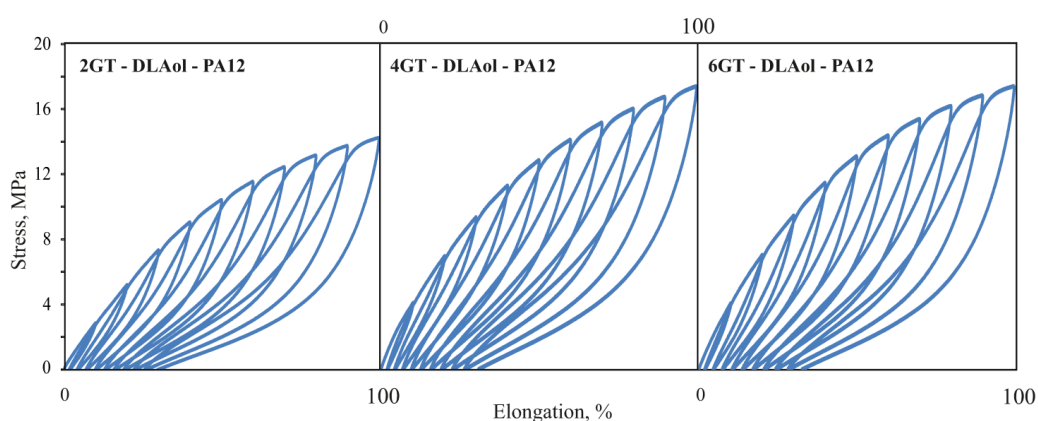


Figure 7. Mechanical hysteresis loops at elongation growing by 10% of the terpoly(ester-aliphatic-amide).

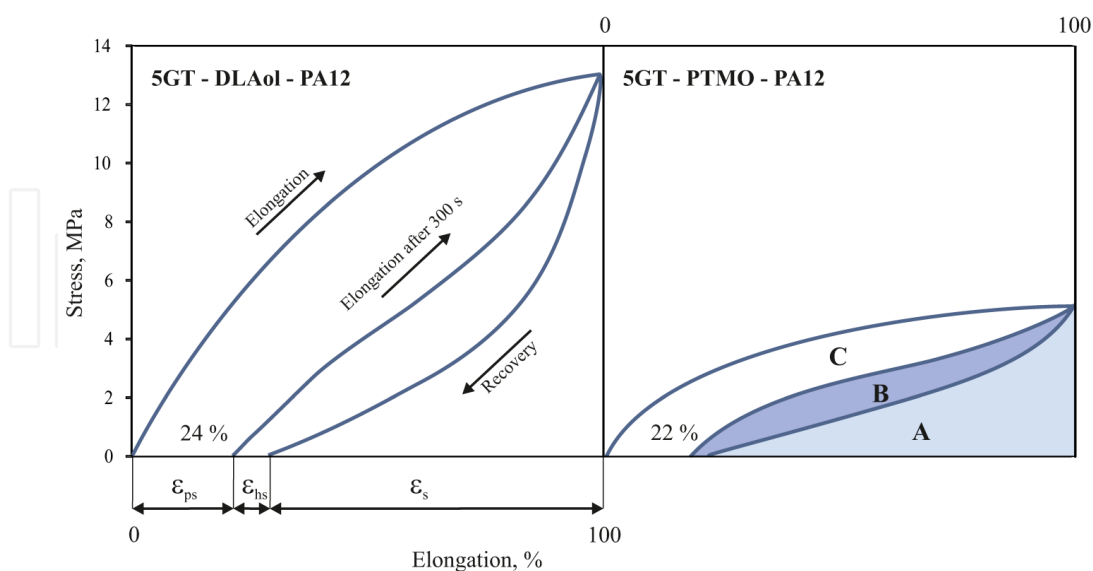


Figure 8. Mechanical hysteresis loops at a constant elongation of 100% of terpoly(ester-aliphatic-amide) and terpoly(ester-ether-amide), where the ester block was 5GT: ϵ_s – elastic elongation, ϵ_{hs} – delayed high-elastic elongation, ϵ_{ps} – permanent set, A – area proportional to the dissipated elastic energy, B – area proportional to the dissipated high-elastic energy, C – area proportional to the accumulated energy.

In both series, the best mechanical properties have the terpolymer with the number $x=4$, whereas the best elastic residues exhibit terpolymers with $x=5$. Better mechanical properties, but worst elastic residues have terpolymers where the amorphous phase is DLAol (series II). This is probably due to the lower weight content of flexible blocks in the terpolymers. Terpolymers of this series, similar to PEE and PEA, exhibit a large part of energy accumulated during the first cycle of elongation. The probable cause is the strong interactions at the domain-matrix contact in these materials, due to hydrogen bonds, Van der Waals forces, or through Chain foldings. The mechanical hysteresis loops of terpoly(ester-ether-amide)s (series I) demonstrate that there is in these materials a small energy accumulation in the first cycle. Therefore, they are elastomers with a better mechanical shape memory than terpoly(ester-aliphatic-amide).

3.5. WAXS analysis

The crystal structure of PTT homopolymer is observed at scattering angles 2Θ of 15.08° , 16.51° , 19.17° , 23.19° , 24.39° , and 26.91° . The most intense diffraction peaks appear in doublets. The diffraction pattern of PA12 homopolymer has one wide diffraction maximum with two extreme points: 20.44° and 21.26° , which are a result of overlapping of the reflections originating from two polymorphic structures γ and α PA12. The terpolymer diffraction patterns exhibit only two reflections with the glancing angles 2Θ corresponding to the angle values on the PA12 diffraction pattern.

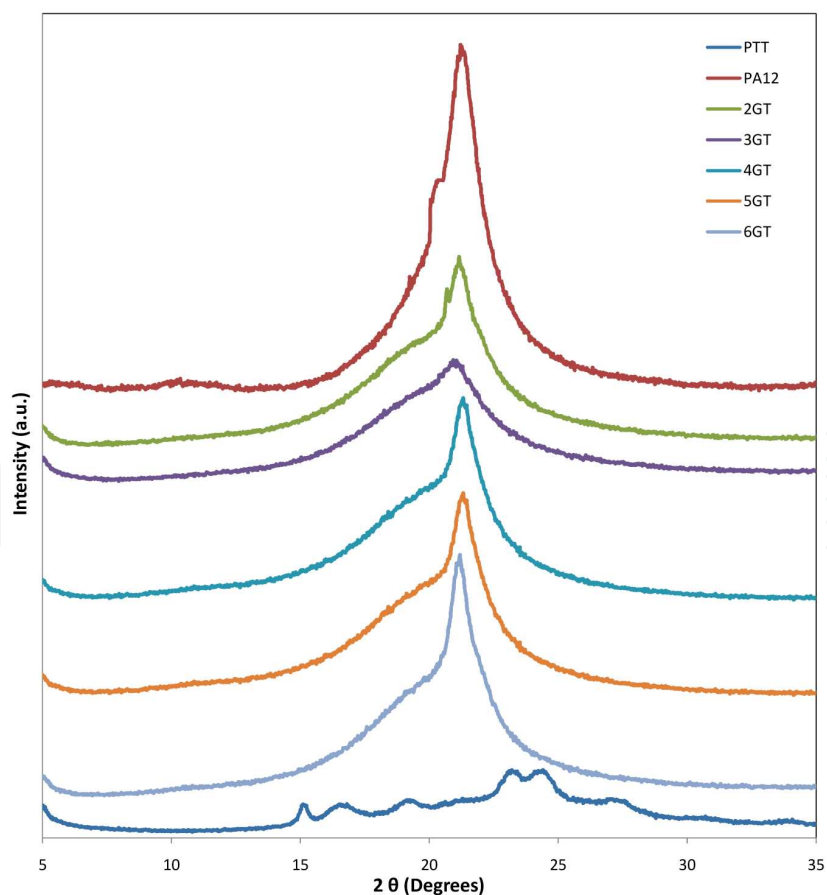


Figure 9. WAXS diffractograms of PTT, PA12, and multiblock terpolymers where the soft phase is DLA.

The qualitative analysis of the diffractograms (Figures 9 and 10) suggests that in the obtained terpolymers composed of the ester and amide hard blocks, only the amide block is responsible for the formation of the crystalline phase. For all the series, terpolymers where the ester block is trimethylene terephthalate exhibits poor-shaped and very wide diffraction maximum. This may indicate the weakest capacity for crystallization of these polymers. There are fewer polymorphic structures γ of PA12 in terpolymers where the matrix is DLAol than in those where the matrix is PTMO.

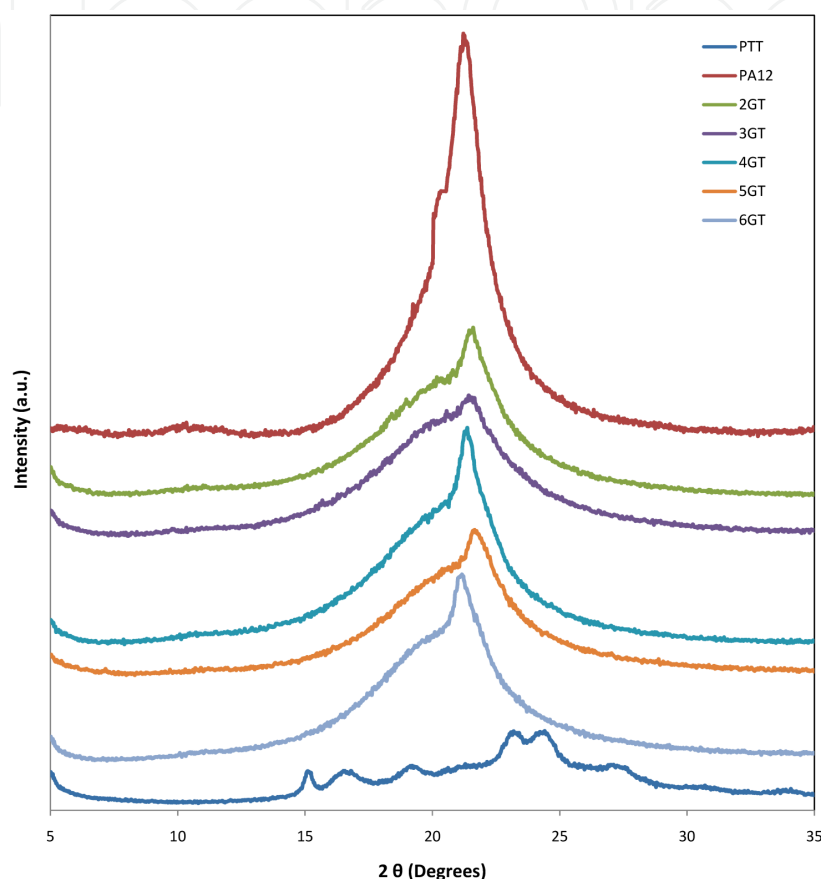


Figure 10. WAXS diffractograms of PTT, PA12, and multiblock terpolymers where the soft phase is PTMO..

3.6. Thermal properties

The terpolymer samples were heated, cooled, and reheated in the temperature range from -90°C to 250°C . The DSC curves of multiblock elastomers can be divided into two parts. The trend of the first part, which is in the low-temperature range of $-90^{\circ}\text{C} < T < 25^{\circ}\text{C}$, characterizes the processes caused by the changes in the soft phase. The trend of the second part of these curves, above 25°C , characterizes the thermal properties of the hard phase. The glass transition temperature T_g , change of specific heat ΔC_p , crystallization temperature T_c , enthalpy of crystallization ΔH_c , melting point T_m , and melting enthalpy ΔH_m for the soft and hard phases in both series of terpolymers was determined. The influence of chemical compositions of ester block on the thermal properties and on the values of phase change temperatures of the products are presented in Table 6 and are shown in Figures 11–16.

Sample	T_{gl} , °C	ΔC_p , J/gK	T_{m1} , °C	ΔH_{m1} , J/g	T_{m2} , °C	ΔH_{m2} , J/g	T_c , °C	ΔH_c , J/g	T_{m3} , °C	ΔH_{m3} , J/g
1	-72	0,18	-5	8	49	1,9	55	14,15	122	12,3
2	-73	0,28	-2	0,21	53	2,14	33	14,66	108	4,32
3	-72	0,16	-1	0,32	61	3,24	59	15,74	133	14,07
4	-73	0,29	4	5,15	53	1,37	60	13,23	127	11,63
5	-79	0,26	4	7,32	59	4,49	76	25,25	133	18,59
6	-21	0,12	-	-	57	3,637	44	14,56	122	13,93
7	-20	0,15	-	-	56	4,156	26	11,75	112	7,236
8	-21	0,13	-	-	55	2,842	53	18,4	130	17,4
9	-21	0,12	-	-	56	4,234	35	13,05	115	10,29
10	-23	0,16	-	-	56	3,349	53	17,57	129	15,67

T_{gl} , T_{m1} – glass transition and melting point temperatures, respectively in low-temperature region; ΔC_p – heat capacity change in T_{gl} ; ΔH_{m1} – heat of melting at T_{m1} ; T_{m2} , T_{m3} , T_c – melting point temperatures and crystallization temperatures, respectively in high-temperature region, ΔH_c – crystallization heat in T_c ; ΔH_{m2} – heat of melting at T_{m2} ; ΔH_{m3} – heat of melting at T_{m3}

Table 6. The DSC study results for terpolymers.

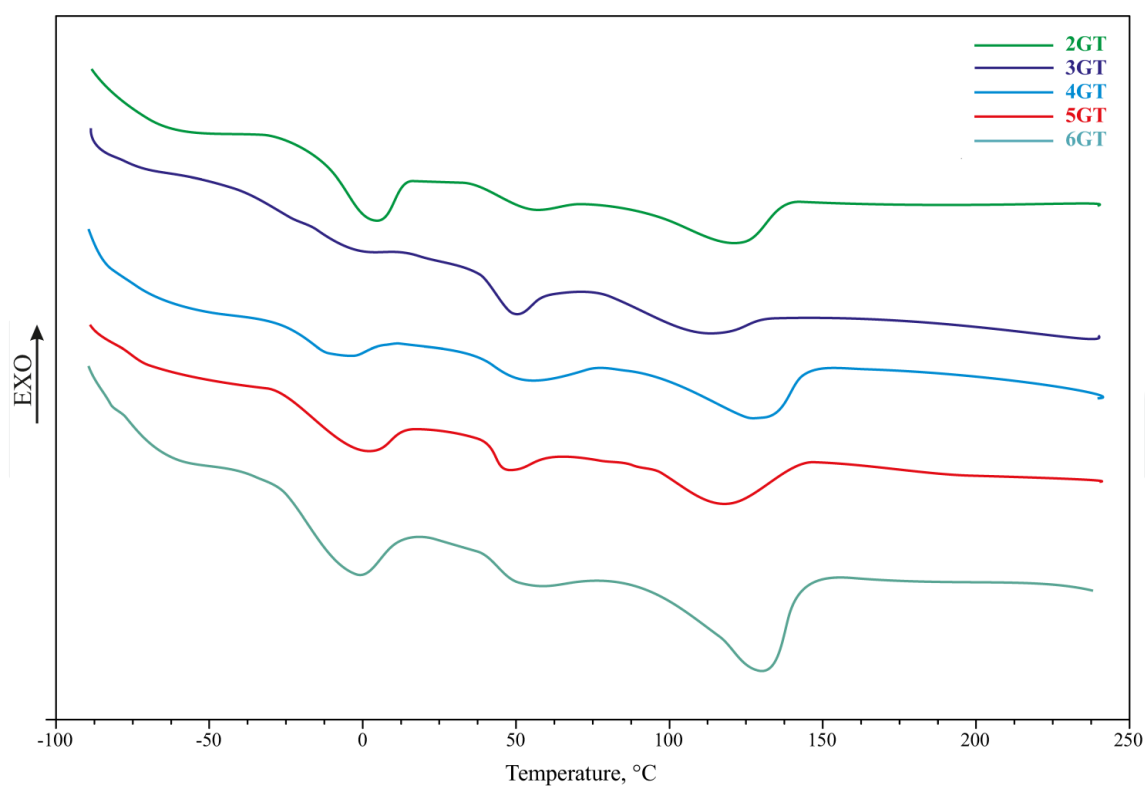


Figure 11. The first heating scans of the terpolymers of series I.

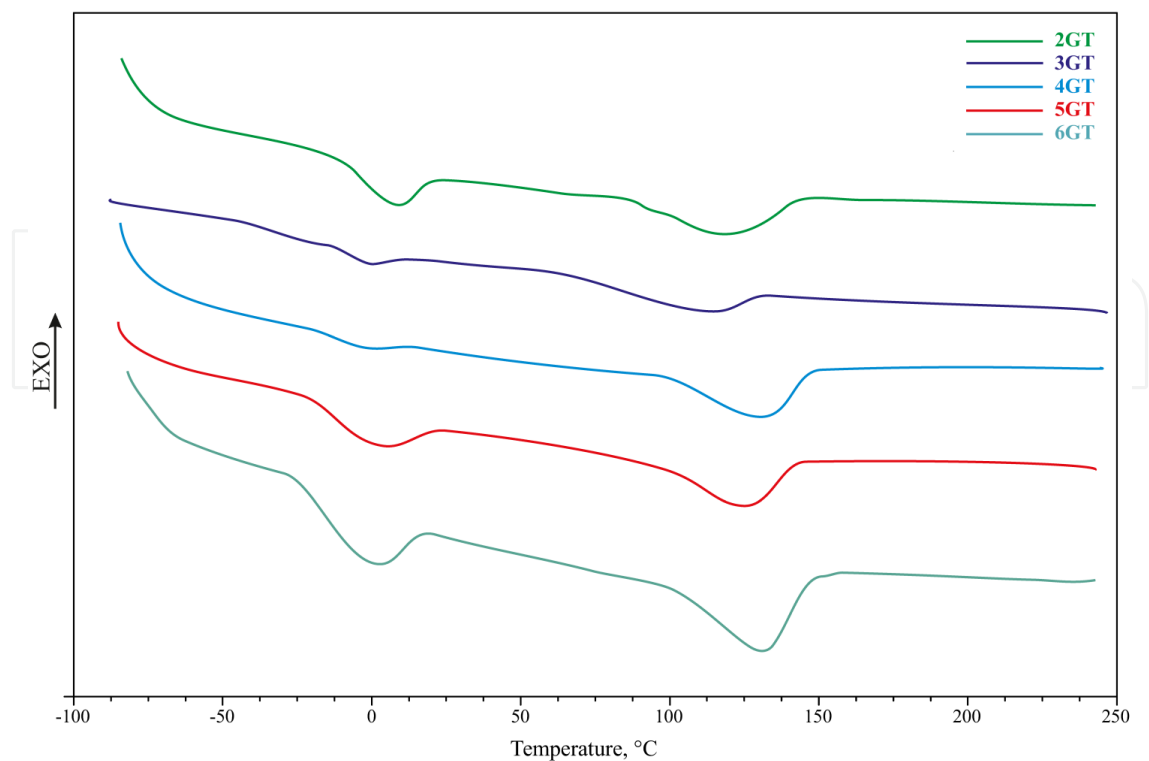


Figure 12. The second heating scans of the terpolymers of series I.

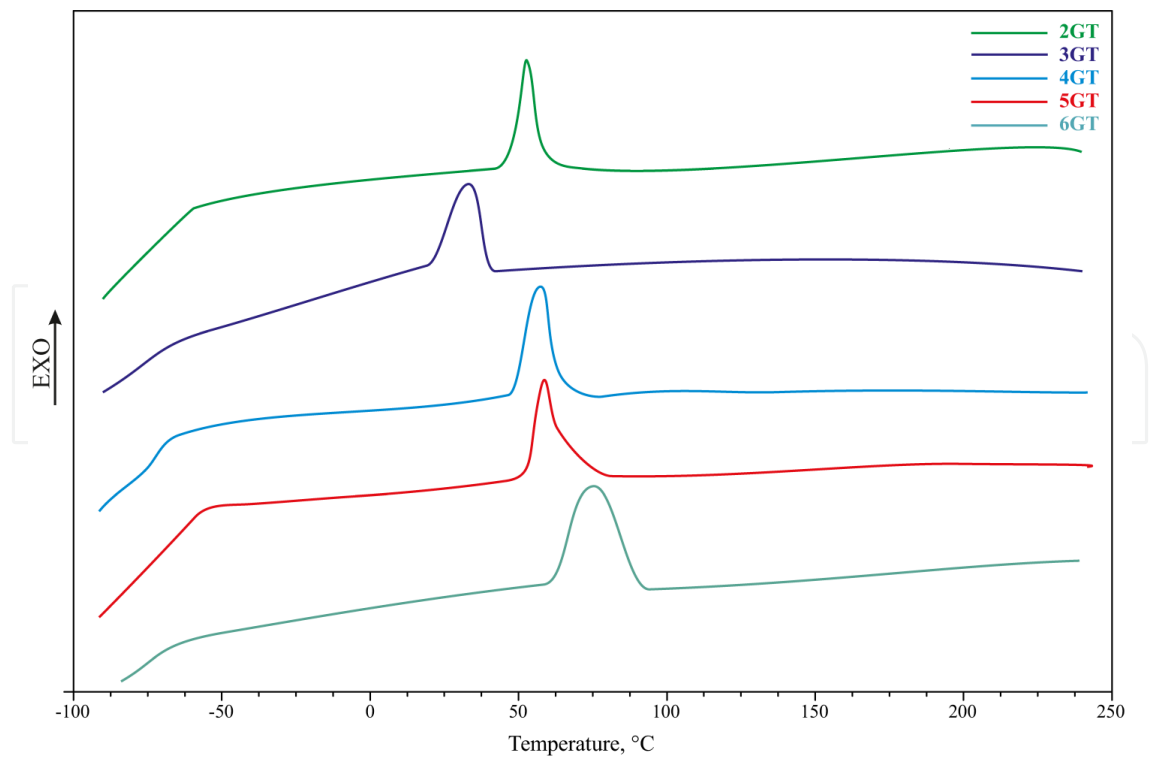


Figure 13. The cooling scans of the terpolymers of series I.

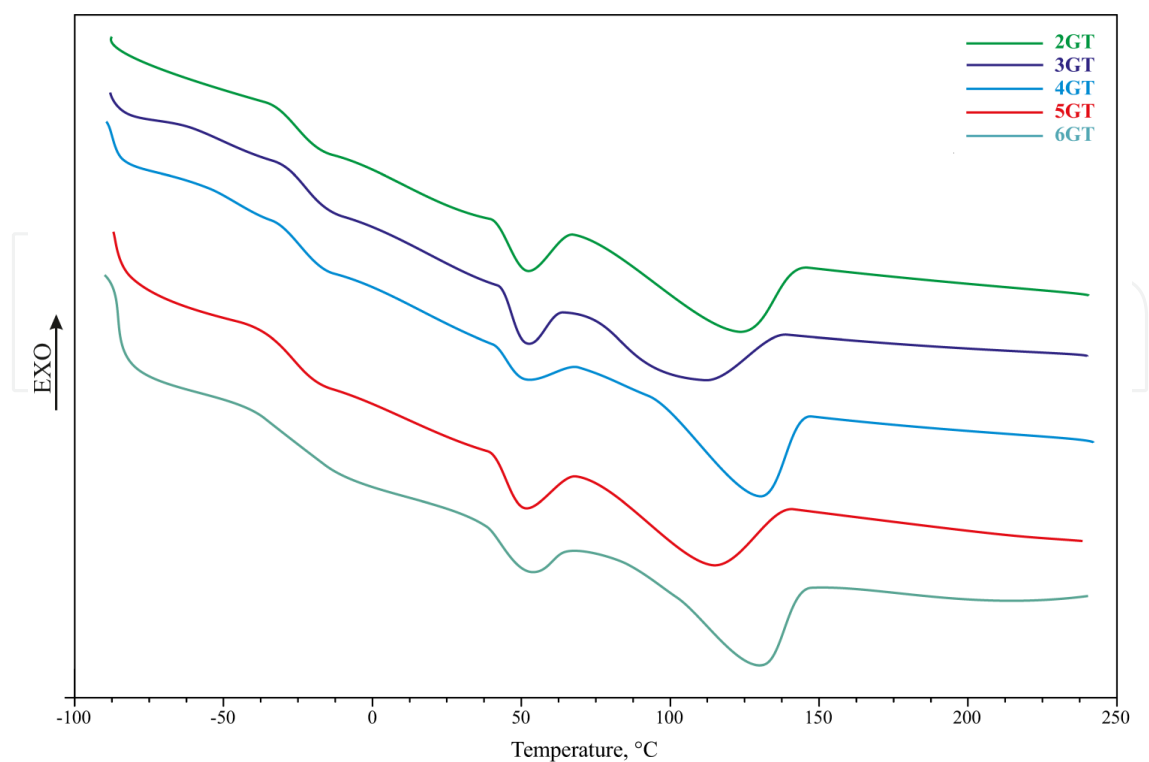


Figure 14. The first heating scans of the terpolymers of series II

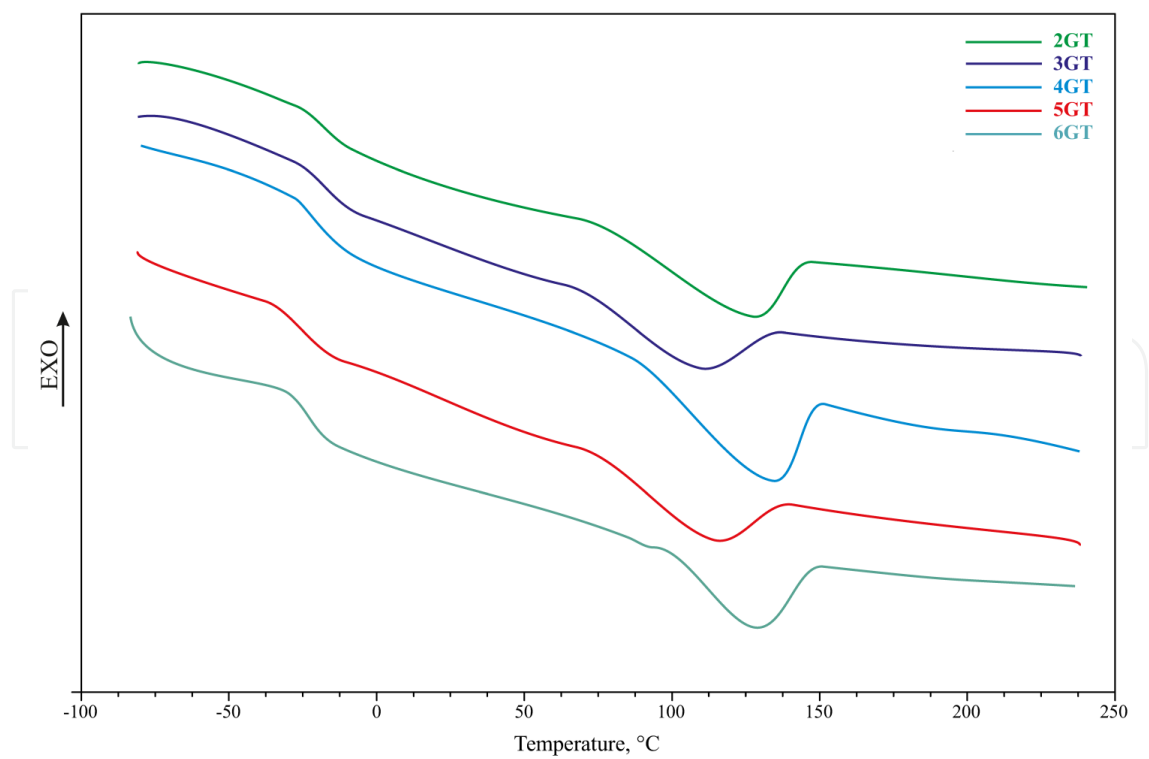


Figure 15. The second heating scans of the terpolymers of series II.

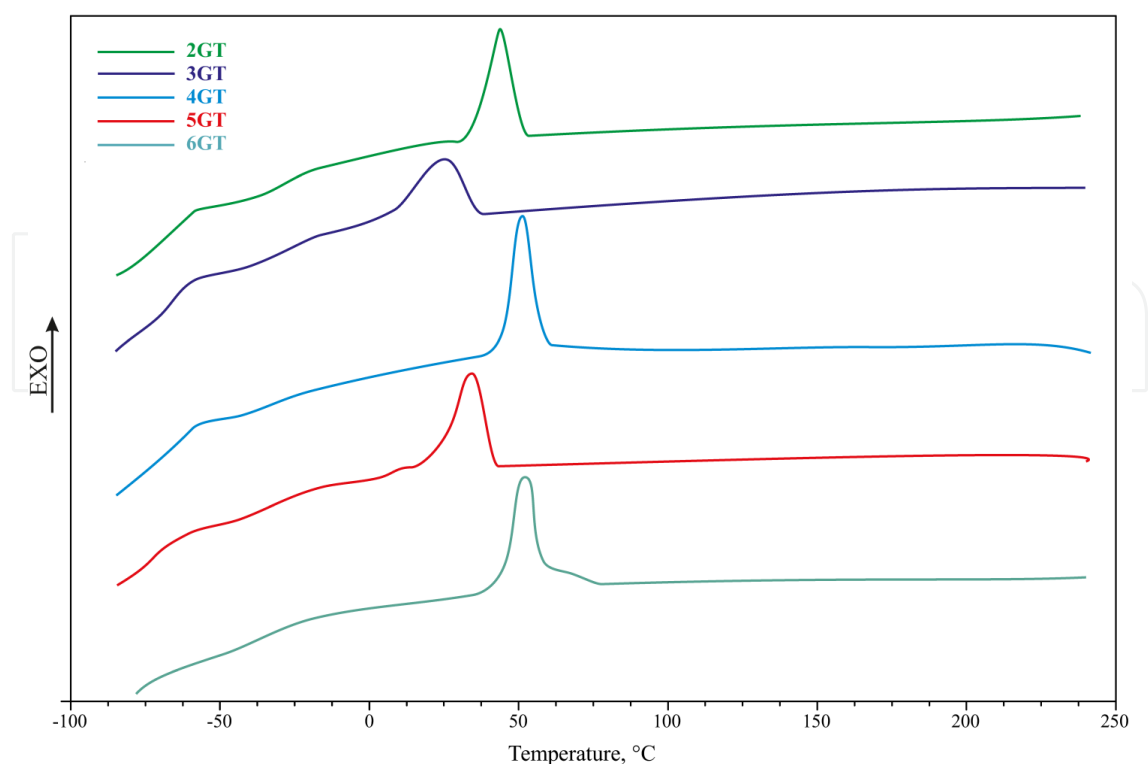


Figure 16. The cooling scans of the terpolymers of series II.

Characteristic for xGT-PTMO-PA12 terpolymers is the constant value of the glass transition temperature ($T_{gPTMO} \approx -72^{\circ}\text{C}$) in the low-temperature region, which is independent of the ester block chemical structure. The glass transition of PTMO homopolymer is -90°C and differs from the obtained terpolymers by 20°C . For the xGT-DLAol-PA12 terpolymers, difference between T_g of flexible block ($T_{gDLAol} \approx 61^{\circ}\text{C}$) and terpolymers is even greater and amounts 40°C . The immobilization of the chain-ends of the flexible block by the chemical bond enhances its T_g of about 5°C – 10°C , and the interaction of the dispersed phase on this block by a further 5°C . The difference between the homopolymer glass transition temperatures and obtained terpolymers received up to 20°C and 40°C , therefore, cannot be explained by immobilization of the chain-ends or by interphase interactions. Probably, further increase in T_{g1} is responsible for the terpolymers dissolution of the short ester sequence in the soft phase. The poor-shaped melting endotherm is observed in the low-temperature region in terpolymers of series I. It determined the heat of fusion of the soft phase. With the increase of the number of carbons separating the terephthalate groups in the ester block of terpolymers also increased the melting point temperature of the crystalline fraction of PTMO blocks. This shows that the purity of the PTMO soft phase increases. In the high-temperature part of the DSC curves two melting endotherms are observed. The first thermal effect, which is called annealing endotherm, is characteristic for many polymers crystallized from the melt and it disappeared during the second heating. It is understood that it accounts for the melting of defected, small crystallites and is associated with the heat of dispersion of the mesomorphic aggregates occurring in terpolymers. The melting point temperature increased with the increasing amounts of the carbons separating the terephthalate groups in the ester block of terpolymers. For the samples with odd number of

carbons x in the ester block, T_m is by 10°C – 15°C lower than in the case of the other terpolymers (principle of parity). The same regularity is observed during cooling of the materials. The difference in the chemical structure of the esters block practically does not influence on the maximal temperature range of application, which is about 200°C .

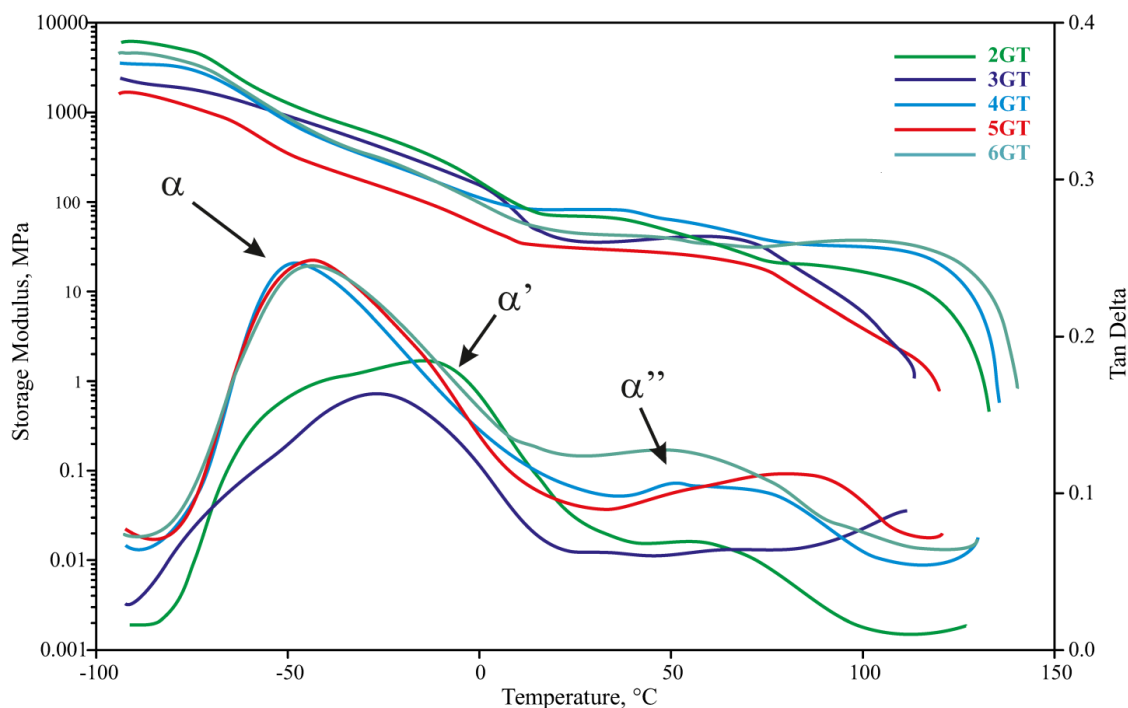


Figure 17. DMTA analysis of the terpolymers of series I.

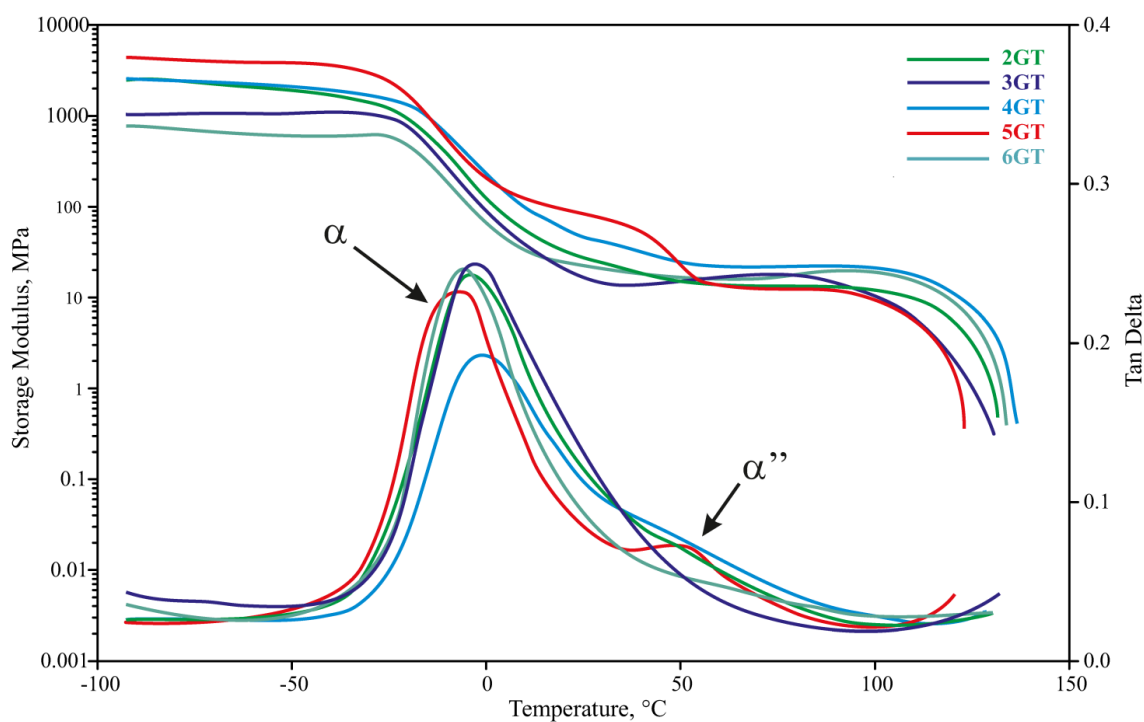


Figure 18. DMTA analysis of the terpolymers of series II.

The effect of temperature on the dynamic mechanical properties of TPEEA depending on the chemical structure of ester block was presented in Figures 17 and 18. The obtained temperature spectra are the curves being characteristic for the thermoplastic elastomers. The spectra of the storage modulus have three temperature regions, in which the courses $E' = f(T)$ differ significantly. In the temperature region from 100°C to -70°C (PTMO) or -20°C (DLAol), the obtained TPEEAs exhibited a constant, characteristic for the glass state, the value of storage modulus above 1 GPa. In the region from -70°C (PTMO) or -20°C (DLAol) to 10°C, a decrease of modulus was observed that was caused by the appearance of viscoelasticity relaxation processes. A further increase of temperature caused the occurrence of a wide “plateau” of elastic state, which at a temperature of 120°C terminates by a rapid lowering at the point of crystallite melting of the hard block phase. For all xGT-PTMO-PA12 samples, the $\tan \delta$ curves possess a broad relaxation peak composed of two relaxation transitions α and α' . They may be linked with the glass transition temperatures for region composed of pure PTMO and mixture of PTMO/xGT of the amorphous phase and interphase. Maximum α'' is a result of the relaxation effect of the amorphous phase of PA12. xGT-DLAol-PA12 terpolymers has one narrow and high damping peak. Probably, in these terpolymers the interphase is smaller because of weak mixing of ester blocks with DLAol matrix.

4. Conclusion

The synthesis, structure, and properties of poly[(multi-methylene terephthalate)-block-(oxytetramethylene)-block-(laurolactam)] and poly[(multi-methylene terephthalate)-block-(linoleic alcohol dimer)-block-(laurolactam)] terpolymers have been reviewed in this chapter. The influence of the number of carbons separating the terephthalate groups of the ester groups in the benzene ring of other blocks and on the properties and structure of these elastomers have been evaluated.

A series of new thermoplastic block elastomers was prepared by melt polycondensation. Synthesis of poly(ester-b-ether-b-amide) terpolymers was a two-step process in the presence of a titanate catalyst. The first step was the transesterification reaction of dimethyl terephthalate and glycol and the esterification reaction of α,ω -dicarboxylic oligo(laurolactam) with oligo(oxytetramethylene)diol or linoleic alcohol dimer, which is taking place simultaneously in another reactor. The second step was polycondensation reaction of two previously prepared intermediate compounds. A detailed description of this synthesis is given in previous papers [36, 37].

^{13}C NMR and FT-IR methods were used to confirm terpolymers assumed chemical structure. Obtained copolymers had all characteristic FT-IR bands for esters, aliphates or ether, and amides. There is no in obtained terpolymers a strong, wide band for the O-H stretch in the region 3300-3000 cm^{-1} , which is observed in FT-IR spectra of pure dicarboxylic oligoamides. It proves that these blocks are built into the copolymer macromolecule. This conclusion is confirmed by the peak presence at 39.56 ppm in ^{13}C NMR spectra.

The degree of phase separation of soft phase and the degree of crystallinity of hard phase was determined by DSC analysis. The interphase size was also estimated, and the occurrence of

the semicrystalline structures was noticed. The DMTA and WAXS methods supplemented these data. It was found that synthesized copolymers exhibit a multiphase (crystalline-amorphous) physical structure. The amorphous phases (matrix) are composed of the flexible blocks PTMO or DLAol that are contaminated by short ester sequences. The crystalline phase (domains) is composed of the hard blocks PA12 and is disordered by admixtures of the xGT blocks. The number of carbons separating the terephthalate groups in the ester block has little effect on the physical properties of the terpolymers obtained by slightly increasing the amorphous phase.

It has been concluded that in both series the best elastic residues have the terpolymer with the number of carbons $x=5$. Probably the interphase of these samples is large and well shaped. Better elastic properties are exhibited by terpolymers of series I, where the soft phase is PTMO because these block is more flexible (large capability for motion and rotation of ether bond).

Obtained terpolymers exhibit unique properties, such as low glass transition temperature, a wide temperature range of application, fast crystallization, good mechanical properties, including good elasticity, thermal stability, and thermal and chemical resistance, and may find application in practice.

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