

# Thermal properties of terpoly(ester-*b*-ether-*b*-amide)s with aliphatic ester blocks

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**Abstract** Two series of multiblock terpolymers, terpoly(ester-*b*-ether-*b*-amide) and terpoly(estersoft-*b*-ether-*b*-amide), with the same type of oligoamide (oligolauro lactam (PA12)) hard block and oligoether (oligoxytetramethylene diol soft block) were obtained. Oligo (butylene sebacate) was used as oligoester soft block in the first series and oligo (butylene dilinoleate) soft block in the second one. The influence of changes in chemical composition of ester block on the thermal of the terpolymers have been determined by differential scanning calorimetry and dynamic mechanical thermal analyses.

**Keywords** Thermoplastic elastomers · Thermal analysis · DSC · DMTA · Mutual miscibility of soft and hard blocks · Phase structure

## Introduction

A part of multiblock terpolymers of the  $-(A_xB_yC_z)_n-$  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 [1–3].

Such heterophase systems are unique in that the dispersed domain structures are thermodynamically stable in the dispersed state. The phase separation in 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 [4, 5].

Two series of multiblock terpolymers—terpoly(ester-*b*-ether-*b*-amide) (TEEA) with the same type of oligoamide (oligolauro lactam (PA12)) hard block and oligoether (oligoxytetramethylene diol (PTMO) soft block) were obtained. Oligo (butylene sebacinate) was used as oligoester block in the first series and oligo (butylene dilinoleate) soft block in the second one.

The influence of changes in chemical composition of ester block on the structure and thermal and mechanical properties of the terpolymers have been determined by differential scanning calorimetry (DSC) and other standard physical methods.

## Subject of examinations

Purpose of paper was to indicate, how a small modification in the chemical structure of only one of the blocks can influence on the thermal, mechanical properties and structure of the multiblock terpolymers. The following terpolymers were selected for such assumed studies:

- *I series*: poly(butylene sebacate-*b*-oxytetramethylene-*b*-lauro lactam)  $-(BS-b-PTMO-b-PA12)_n-$ ,
- *II series*: poly(butylene dilinoleate -*b*-oxytetramethylene-*b*-lauro lactam)  $-(BDL-b-PTMO-b-PA12)_n-$ .

Two series of multiblock terpolymers, TEEA  $-(BS-b-PTMO-b-PA12)_n-$  and  $-(BDL-b-PTMO-b-PA12)_n-$ , with the

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same type of oligoamide—oligolauro lactam (PA12)—hard block and oligoether—oligoxytetramethylene diol (PTMO)—soft block and different oligoester blocks were obtained.

In the first series, oligo(butylene sebacate) was used as oligoester block (BS) prepared by esterification reaction of sebacic acid (SA) with 1,4-butanediol (BD-1,4) and oligo(butylene dilinoleate)(BDL) block derived from saturated dilinoleic acid (DLA) and 1,4-butanediol (BD-1,4) in the second one.

The influence of changes in chemical composition of ester blocks on the thermal properties of the terpolymers have been determined by DSC and other standard physical methods. Syntheses of the oligoamide PA12 blocks and terpolymers  $-(BS-b-PTMO-b-PA12)_n-$ ,  $-(BDL-b-PTMO-b-PA12)_n-$  were previously described in details [6, 7].

## Methods

The differential calorimetric method was recorded on a DSC-910 (DU Pont Instruments) apparatus. The samples were examined in a triple cycle (heating–cooling–heating) in the temperature range from  $-100$  to  $+220$  °C. The heating and cooling rates were  $10$  °C  $\text{min}^{-1}$ .

The dynamical mechanical analysis (DMA) was performed on a DMA Q-800 modulus (TA-Instruments) in the temperature range from  $-100$  to  $+125$  °C at  $35$  Hz. The storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$  were determined.

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

The limiting viscosity number ( $[\eta]$ , LVN) of the poly[ether-*b*-ester-*b*-amide] terpolymers in phenol-trichloroethylene (50:50 vol%) was determined by an Ubbelohde viscometer IIA at  $30$  °C.

## Results and discussion

Description and properties of terpolymers is summarized in Table 1.

The DSC 2nd heating and cooling scans for poly (oligo(butylene sebacate-*b*-oxytetramethylene-*b*- lauro lactam)  $-(BS-b-PTMO-b-PA12)_n-$ , and poly(butylene dilinoleate-*b*-oxytetramethylene-*b*-lauro lactam)  $-(BDL-b-PTMO-b-PA12)_n-$  are shown in Figs. 1, 2, and the thermal properties of the terpolymers of both series are given in Table 2.

The endotherms connected with melting transition of PA12 ( $T_{m3}$ ) can be observed on DSC curves for first series (Fig. 1), they decrease and flatten along with an increase of degree of polymerization for butylene sebacate.

Crystalline structure of PA12 is disturbed, what can be interpreted as a solution of this block in phase created by other blocks. Similar situation can be observed for melting temperature transition of oligoether segments ( $T_{m1}$ ), which decreases with increasing oligoester content in polymer. For terpolymer with  $DP_{BS} = 7$ , melting transition temperatures ( $T_{m2}$ ) appears on thermograms. Glass transition temperature  $T_g$  increases with increase of soft oligoester molecular weight, which can be connected with their solubility in oligoether phase. Effects of crystallization of oligoamide ( $T_{c3}$ ), oligoester ( $T_{c2}$ ), and oligoether ( $T_{c1}$ ) blocks are presented on cooling curves.

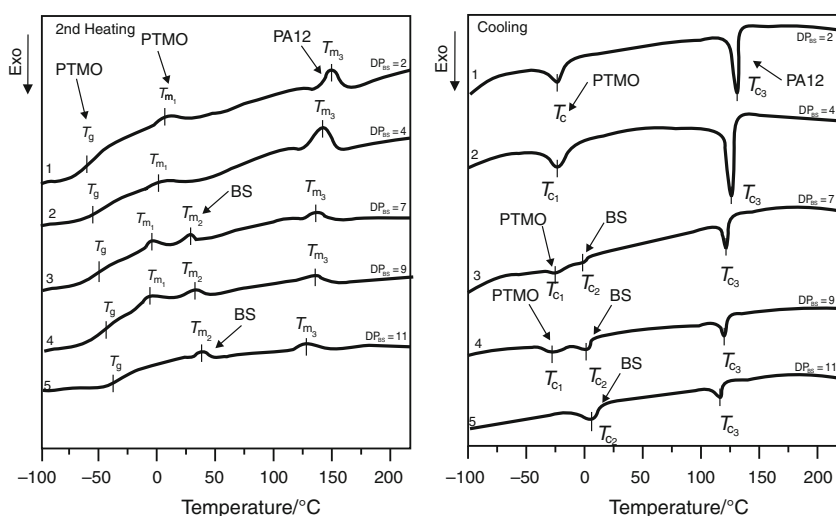
DSC curves of BDL series are present on Fig. 2. For these polymers  $T_{m3}$  connected with crystalline phase of PA12 is almost constant for  $DP_{DLA} = 2-7$  and for  $DP_{DLA} = 9$  immediately decrease. This phenomenon appears distribution of crystalline phase block PA12 by PTMO which solution in this phase in the same time enthalpy decrease. Confirmation of this disappeared of  $T_{m1}$  from PTMO. Analogous observations are presented on cooling curves ( $T_{c1}$ ,  $T_{c3}$ ).  $T_{m2}$  related with DLA is not observed because this block is completely amorphous.

**Table 1** Description and properties of  $-(BS-b-PTMO-b-PA12)_n-$ , and  $-(BDL-b-PTMO-b-PA12)_n-$  terpolymers

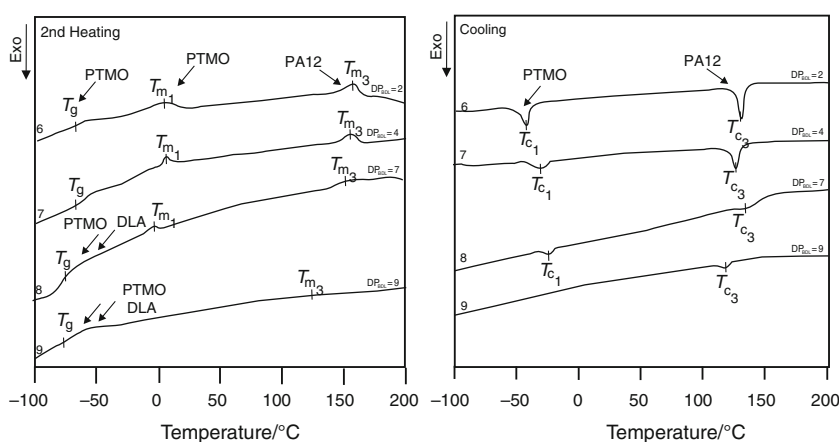
Polymer sample	Molar composition				$[\eta]$ dl/g	H ShD	$DP_{BS}$	Series
	PTMO	PA12	KS	1,4-butandiol				
1	2	1	3	5	0.35	40.8	2	I
2	2	1	5	9	0.37	34.1	4	I
3	2	1	8	15	0.3	31.8	7	I
4	2	1	10	19	0.28	31	9	I
5	2	1	12	23	0.35	32.1	11	I
			DLA				$DP_{BDL}$	
6	2	1	3	5	0.227	21	2	II
7	2	1	5	9	0.228	11	4	II
8	2	1	8	15	0.206	14.7	7	II
9	2	1	10	19	0.172	14.3	9	II

Notations were explained in experimental part

**Fig. 1** DSC thermograms of  $-(BS-b-PTMO-b-PA12)_n-$  terpolymers characterized by different polymerization degree of polyester block  $DP_{BS}$  subjected to heating and cooling



**Fig. 2** DSC thermograms of  $-(BDL-b-PTMO-b-PA12)_n-$  terpolymers characterized by different polymerization degree of polyester block  $DP_{BDL}$  subjected to heating and cooling



Glass transition temperature  $T_g$  decreased with increasing of  $DP_{BDL}$  (DLA content), which can indicate miscibility of the both soft blocks (DLA and PTMO). Evidenced by the increase in glass transition range and the associated increase in heat capacity  $\Delta c_p$ .

Changes of  $T_{m_3}$  of PA12 for both series are presented on Fig. 3c. For BS series we can observe monotonic decrease with increasing of BS content.

Terpolymers from series based on DLA have higher melting temperatures  $T_{m_3}$  PA12 than series BS but only to  $DP = 7$  and after this value rapidly falls. BS is crystalline and miscibility with PA12 crystalline (from  $DP = 2-11$ ) in whole range of composition, hence we can observe constant decrease with increasing  $DP_{BS}$ . Whereas DLA content promotes crystallization of oligoamide and the above limiting value  $DP = 7$  completely disorders crystalline phase. Melting temperatures related with PTMO presented on Fig. 3b are observed only for terpolymers to  $DP = 7$  for DLA series and to  $DP = 9$  for BS series. For both series  $T_{m_1}$  visibly decreases but for DLA series values are lower.

Interesting changes of  $T_g$  of soft phase are present on Fig. 3a. Temperatures of “pure” substrates are BS is  $-65$  °C, DLA is  $-68$  °C, and PTMO is  $-90$  °C.

$T_g$  for BS series increase from  $-64$  to  $-44$  °C because amorphous parts of all components of terpolymers are miscibility. With increasing  $DP_{BS}$  relatively decrease PTMO content and components with higher  $T_g$  start to play a part. For DLA,  $T_g$  is resultant of amorphous phase ( $T_g$  from  $-72$  to  $85$  °C). Almost all PTMO for crystalline phase come into amorphous phase that  $T_g$  decrease. PTMO is dominant in soft phase [8, 9].

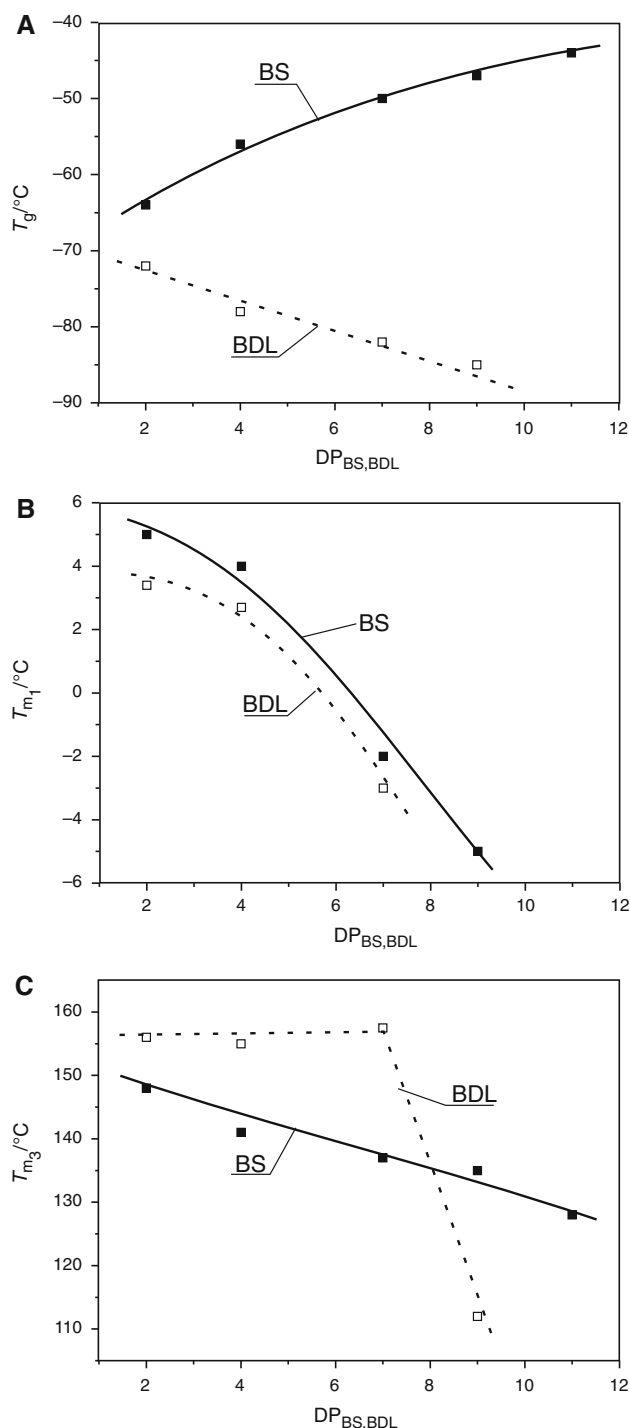
Figures 4, 5 show the results of dynamic mechanical thermal analysis. The relaxation behavior of all samples was studied by DMTA, measurements of the storage modulus  $E'$ , the loss modulus  $E''$ , and the loss tangent  $\tan \delta$  as a function of the temperature.

Spectra of storage modulus  $E'$  of terpolymers  $-(BS-b-PTMO-b-PA12)_n-$  (Fig. 4) characterize different temperature ranges, where values of  $E'$  change with the change of the degree of polymerization of BS hard block.

**Table 2** Thermal properties of the  $-(BS-b-PTMO-b-PA12)_n$  and  $-(BDL-b-PTMO-b-PA12)_r$ - terpolymers

Sample	$DP_{BS}$	$T_g/^\circ C$	$\Delta C_p/J/g K$	Soft blocks				Hard blocks							
				Oligoether		Oligoester		Oligoether		Oligoamide					
				$T_{m1}/^\circ C$	$\Delta H_{m1}/J/g$	$T_{c1}/^\circ C$	$\Delta H_{c1}/J/g$	$T_{m2}/^\circ C$	$\Delta H_{m2}/J/g$	$T_{c2}/^\circ C$	$\Delta H_{c2}/J/g$	$T_{m3}/^\circ C$	$\Delta H_{m3}/J/g$	$T_{c3}/^\circ C$	$\Delta H_{c3}/J/g$
1	2	-64	0.567	5	23.8	-24	22.8	-	-	-	-	148	29.6	128	28.8
2	4	-56	0.532	4	13.1	-25	12.8	-	-	-	-	141	19.9	118	19.2
3	7	-50	0.534	-2	13.7	-26	13.5	31	10.2	-4	9.8	137	9.9	117	9.3
4	9	-47	0.521	-5	9.4	-27	9.2	35	12.5	0	11.8	135	9	115	8.7
5	11	-44	0.509	-	5.7	-	5.2	38	13.8	4	13.2	128	6.3	114	5.9
Sample	$DP_{BDL}$	$T_g/^\circ C$		Soft blocks				Hard blocks							
				Oligoether		Oligoester		Oligoether		Oligoamide					
				$T_{m1}/^\circ C$	$\Delta H_{m1}/J/g$	$T_{c1}/^\circ C$	$\Delta H_{c1}/J/g$	$T_{m2}/^\circ C$	$\Delta H_{m2}/J/g$	$T_{c2}/^\circ C$	$\Delta H_{c2}/J/g$	$T_{m3}/^\circ C$	$\Delta H_{m3}/J/g$	$T_{c3}/^\circ C$	$\Delta H_{c3}/J/g$
6	2	-72	0.553	3.4	15	-43	14.3	-	-	-	-	156	18	130	17.6
7	4	-78	0.649	2.7	7	-38	6.8	-	-	-	-	155	11	127	10.6
8	7	-82	0.756	-3	3	-32	2.6	-	-	-	-	157.5	4	128	3.8
9	9	-85	0.864	-	-	-	-	-	-	-	-	112	1.9	117	1.7

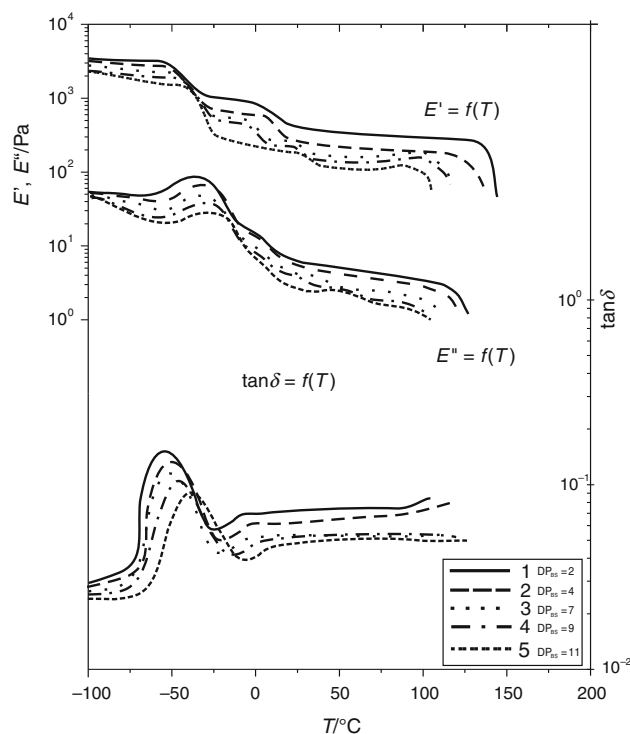
$T_g$  glass transition temperatures of soft blocks,  $\Delta C_p$  capacity heat,  $T_{m1}$  melting temperatures of oligoether blocks,  $T_{m2}$  melting temperatures in oligoester blocks,  $T_{m3}$  melting temperatures of oligoamide hard blocks,  $T_{c1}$  crystallization temperatures of oligoether blocks,  $T_{c2}$  crystallization temperatures of oligoester blocks,  $T_{c3}$  crystallization temperatures of oligoamides blocks,  $\Delta H_{m1}$ ,  $\Delta H_{m2}$ ,  $\Delta H_{m3}$  heat of melting at  $T_{m1}$ ,  $T_{m2}$ ,  $T_{m3}$ ;  $\Delta H_{c1}$ ,  $\Delta H_{c2}$ ,  $\Delta H_{c3}$  crystallization heat in  $T_{c1}$ ,  $T_{c2}$ ,  $T_{c3}$



**Fig. 3** Changes of  $T_g$ ,  $T_{m1}$ ,  $T_{m3}$  of  $-(BS-b-PTMO-b-PA12)_n-$ ,  $-(BDL-b-PTMO-b-PA12)_n-$  terpolymers with various polymerization degree of  $DP_{BS,BDL}$

In the temperature range from  $-100$  to  $-50$  °C functions  $E'' = f(T)$  have a flat course, the modulus does not change and  $-(BS-b-PTMO-b-PA12)_n-$  is in the glassy state.

In the interval from  $-50$  to  $-25$  °C modulus decreases, and in the macromolecules there is viscoelastic relaxation



**Fig. 4** The storage modulus  $E'$ , the loss modulus  $E''$ , and the loss tangent  $\tan \delta$  of  $-(BS-b-PTMO-b-PA12)_n-$  terpolymers versus temperature

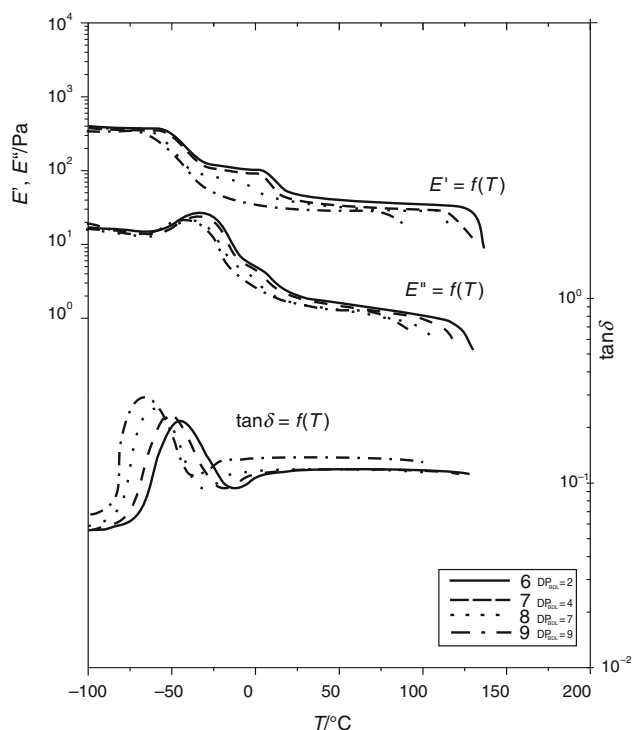
processes connected with the glass transition of amorphous phase of the PTMO soft block. This interval moves toward higher temperatures with increasing degree of polymerization of  $DP_{BS}$ . The third temperature range is a “flexibility plateau”, where the modulus in this interval is constant. The fourth region observed in the temperature range  $0$ – $25$  °C is characterized by a further slight decrease of the modulus associated with the melting of the crystalline phase transformation of the PTMO soft block.

With increasing degree of polymerization of the BS block, the width of this range decreases and shifts toward lower temperatures.

For the terpolymer with degree of polymerization  $DP_{BS} = 11$  melting transition of the PTMO soft block is not observed, which was confirmed in the DSC studies.

In the temperature range of  $25$ – $50$  °C for the terpolymer with a degree of polymerization 7, we can observe a slight decrease of the modulus connected with the melting point of a hard block of BS. The width of this range increases with increasing concentration of BS in terpolymer and is moving toward higher temperatures, which was also confirmed by results of DSC investigation. In the temperature range of  $80$ – $130$  °C terpolymers achieve the predominance of viscous on elastic properties and their storage modulus is rapidly declining.

Inflection on the curves related to this decrease determine the temperature of polymer softening, and therefore also the



**Fig. 5** The storage modulus  $E'$ , the loss modulus  $E''$ , and the loss tangent  $\tan \delta$  of  $-(BDL-b-PTMO-b-PA12)_n-$  versus temperature

upper temperature range of applicability decrease with the increase of terpolymer  $DP_{BS}$ . On the curves  $E'' = f(T)$  and  $\tan \delta = f(T)$   $-(BS-b-PTMO-b-PA12)_n-$ , there is a maximum of  $\alpha$  relaxation associated with glass transition temperature of PTMO overlapping with the results of DSC. With the increase of concentration of BS block these peaks flatten and shift toward higher temperatures.

Spectra of storage modulus  $E'$  terpolymers  $-(BDL-b-PTMO-b-PA12)_n-$  (Fig. 5) in comparison to terpolymers  $-(BS-b-PTMO-b-PA12)_n-$ , are characterized by lower values, while also we can observe the influence of variable of the degree of polymerization  $DP_{BDL}$  on the range of temperature intervals.

In the temperature range of  $-100$  to  $-70$  °C functions  $E' = f(T)$  have a flat course, the modulus does not change and  $-(BDL-b-PTMO-b-PA12)_n-$  is in the glassy state.

In the interval from  $-70$  to  $-25$  °C a decrease of modulus follows, and in macromolecules viscoelastic relaxation processes occur, which is related with the glass transition of amorphous phase within the PTMO soft block. With increasing degree of polymerization of BDL block, the width of this interval increases and shifts toward lower temperatures. The third temperature range is a “flexibility plateau,” the modulus in this interval is constant. The fourth range observed in the temperature range  $0$ – $25$  °C is characterized by a further slight decrease of modulus connected with melting transition of the

crystalline phase of the PTMO soft block. With increasing degree of polymerization of BDL block, the width of this range decreases and shifts toward lower temperatures. For the terpolymer with a degree of polymerization  $DP_{BS} = 9$  melting transition of PTMO soft block is not observed, which was also confirmed in the DSC results. In the temperature range from  $-70$  to  $140$  °C terpolymers achieve predominance viscous over elastic properties and their modulus is rapidly decreasing. Inflection on the curves related to this decrease determine the polymer softening temperature, and therefore its upper temperature range of applicability decrease with the increase in terpolymer  $DP_{BDL}$ .

On the curves  $E'' = f(T)$  and  $\tan \delta = f(T)$   $-(BDL-b-PTMO-b-PA12)_n-$  there is maximum of relaxation  $\alpha$  associated with PTMO glass transition temperature, overlapping with the results of DSC. With the increase of concentration block BDL these maxima broaden and shift toward lower temperatures. This is a confirmation of test results obtained by DSC, where it was found to increase amorphous phase associated with the miscibility of phases derived from PTMO and DLA.

## Conclusions

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

The terpolymers  $-(BS-b-PTMO-b-PA12)_n-$  comprise the systems in which the oligo(butylene sebacate (BS) component with  $DP_{BS}$  from 2 to 11 dissolves both in the phase of PA12 blocks (hard) and the phase of PTMO blocks (soft). Structure phase in these systems is highly disturbed. Amorphous BS and DLA are miscible with amorphous PTMO while crystalline PTMO are not miscible with crystalline PA12 and crystalline BS is miscible with crystalline PA12.

The terpolymers  $-(BDL-b-PTMO-b-PA12)_n-$  comprise the systems in which the oligo (BDL) component with  $DP_{BS}$  from 2 to 9 are not miscible with crystalline PA12.

Using of two soft blocks in terpolymers deteriorates mechanical properties because of increase of amorphous phase and decay of crystalline phase.

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