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Synthesis of block polyesteretheramide terpolymers

Summary — The results of studies on the synthesis of triblock condensation polymers were presented. Block polyesteretheramide terpolymers (TPEEA) consisting of a flexible oligooxytetramethylene (PO) block with glass transition point below 0°C and the following hard blocks: oligotetramethyleneterephthalate (PE) and oligo-ε-caprolactam block, both with glass transition points above room temperature, were prepared. These terpolymers were synthesized with the use of PE blocks of molecular weight 1500, 2000, 3000 and 4000 and with the content of these blocks in the range of 10 to 30 mass-%. The content of PO block was also changed in the range of 0 to 60 mass-%. The dependences of the course and results of polycondensation of these triblock polyesteretheramides on the molecular weight and content of PA and PO blocks were obtained.

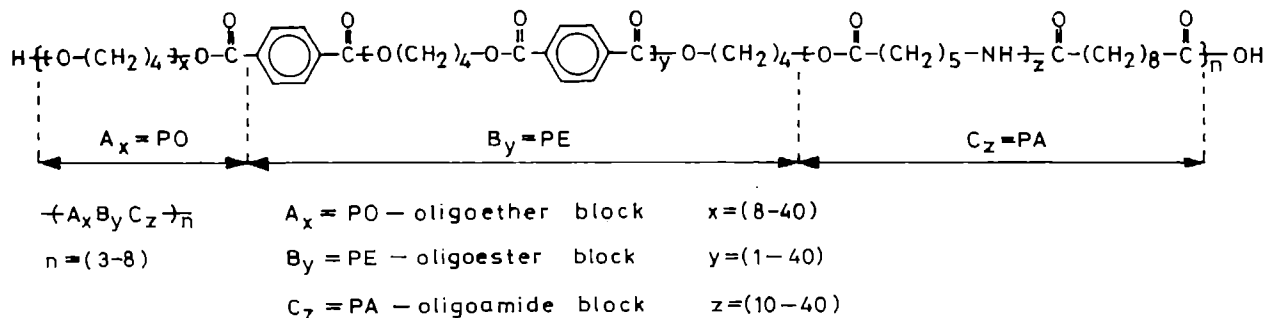
Terpolyesteretheramides (TPEEA) are block polymers of the $(A_x B_y C_z)_n$ type. A macromolecule of this terpolymer consists of two hard blocks with $T_g > 0$ (an oligoester block, PE, capable of crystallization and an oligoamide block, PA, capable of formation of hydrogen bond domains) and of one soft (flexible) block with $T_g < 0$ (an amorphous oligoether block, PO). The theoretical structure of a TPEEA molecule can be represented by formula I.

The idea of synthesizing TPEEA is the consequence of a long research work of the author in the field of copolyesterethers (KPEE) [1–8] and copolyetheramides (KPEA) [9–10] syntheses. The initial stage of TPEEA synthesis was a typical synthesis of a copolyesterether from dimethyl terephthalate (DMT), 1,4-butanediol and oligooxytetramethylenediol (PTMO) with an addition of α,ω-dicarboxylic oligocaprolactam (OKL). Thus, it can be assumed that the synthesis of TPEEA consists in the modification of KPEE with a dicarboxylic amide block.

EXPERIMENTAL

Preparation of α,ω-dicarboxylic oligo-ε-caprolactam

The main unit of the equipment for the condensation polymerization process of ε-caprolactam was a 6-l cylindrical „pressure-vacuum” reactor with a conical bottom made of stainless steel. The height/diameter (h/d) ratio of the reactor was 3.5. In the reactor's cover there were situated: two valves, one for introducing nitrogen and another, a pressure reducing valve; connector pipes for dosing the reactants, and stuffing-boxes; a thermocouple for measuring the temperature inside the reactor; and the shaft of a horseshoe stirrer. Reactor was heated by a set of three resistance heaters with temperature control in the range of 20–400°C and measured with the use of Fe–constantan thermocouples and Pt-100 thermoresistors. The velocity of the variable-speed stirrer was changed smoothly in the range of 100–



800 r.p.m. The whole reactor unit was designed and constructed at the Laboratory of Elastomers and Chemical Fibres Technology at the Technical University of Szczecin.

The hydrolytic condensation polymerization of dicarboxylic oligocaprolactam (OKL) was carried out as follows: Into the reactor purged with nitrogen was introduced ϵ -caprolactam (KL), water (an activator) and sebacic acid (a molecular weight stabilizer). The reaction mixture was heated to 265°C. During the heating period, the pressure in the reactor increased gradually and was kept constant at 0.8 MPa with a continuous removal of H₂O/KL vapours. The pressure of 0.8 MPa was maintained for 60 min. Then, the pressure was reduced during 20 min to normal value. The condensation polymerization was continued under normal pressure and with a weak stream of nitrogen for 180 min at 265°C. After that period of time, the pressure was reduced to about 200 hPa and kept at this value for about 20 min. During the whole process the reaction mixture was stirred vigorously at 100 r.p.m.

When the reaction came to an end, the reaction mass was extruded by means of compressed nitrogen into water, which was intensely stirred in a tub with compressed air from nozzles placed at the tub's bottom. Then, polymer was extracted several times with hot water, washed with hot distilled water, dried and powdered with a specially designed worm crusher. The dried and disintegrated oligoamide was stored in airtight containers. A representative sample was tested and the following values were determined:

- content of end-groups (-COOH and -NH₂),
- melting point and
- limiting viscosity number (LVN or $[\eta]$).

In this manner, α,ω -dicarboxylic oligo- ϵ -caprolactams (OKL) with the theoretically expected molecular weights of 1500, 2000, 3000, and 4000 were prepared. The composition of reactants and the results of analyses for these OKL are given in Table 1.

Preparation of terpolyesteretheramides

The apparatus used in the synthesis of TPEEA was of own design and construction and comprised the following units and systems:

- a stainless-steel reactor for an ester exchange reaction equipped with a horseshoe stirrer, with the total capacity of 3.6 dm³ and the useful capacity of 1.2–1.6 dm³,
- a stainless-steel rectifier and condenser,
- a nitrogen drying and dosing system,
- a heating system with the temperature control for the range of 20–400°C with an accuracy to 2°C,
- a driving system: a.c. motor of 1.1 kW, stirrer velocity of 120 r.p.m.,
- a high-vacuum stainless-steel reactor with a stirrer for the polycondensation reaction with the total capacity of 3.6 dm³ and with the useful capacity of 1.2–1.6 dm³,
- a vacuum system comprising: vacuum valve, pressure reduction valve, and a vacuum pump,
- an electrical heating system with temperature control,
- a driving system comprising: a 0.3 kW d.c. motor with a variable-speed stirrer for the range of 0–120 r.p.m.

Synthesis of TPEEA terpolymers is a three-step process. The first step is the transesterification reaction of dimethyl terephthalate (DMT) and 1,4-butanediol. The second step, taking place simultaneously in another reactor, is the esterification reaction of α,ω -dicarboxylic oligo- ϵ -caprolactam with oligooxytetramethylenediol. The third step is the polycondensation reaction of these two previously prepared intermediate compounds [11, 12]. The course and parameters of the synthesis are presented in the block diagram.

Course of the synthesis processes

As a measure of the advancement of the polycondensation reaction, the increase in LVN values during syn-

Table 1. PROPERTIES AND COMPOSITION OF A SERIES OF OKL RESINS

No. of sample	Symbol	Composition of reactants		Results of analyses						
		ϵ -caprolactam [g]	Sebacic acid [g]	C _{-COOH} [val/T]	C _{-NH₂} [val/T]	η_{rel}	T_i [°C]	Molecular weight (theor.)	Molecular weight from viscometry	Molecular weight from end-groups
1	OKL-1500	3000	467.5	1260	22	1,141	194–200	1500	1595	1560
2	OKL-2000	3000	337.5	969	21	1,178	196–202	2000	2010	2020
3	OKL-3000	3000	216.85	665	26	1,282	207–211	3000	3185	2880
4	OKL-4000	3000	159.75	475	18	1,370	218–222	4000	4180	4320

Explanations:

η_{rel} — relative viscosity, according to PN83/C-89039;

C_{-COOH} — concentration of carboxylic groups: solution of OKL in a phenol-ethanol mixture is titrated with 0.02 N HCl in the presence of thymol blue to change of colour to pink-violet;

C_{-NH₂} — concentration of amine groups: solution of OKL in benzyl alcohol, titration with 0.02 N NaOH in the presence of phenolphthalein to change of colour to pink;

T_i — melting point was determined with the Boëtius apparatus at a heating rate of 2°C/min.

thesis was taken. The LVN was determined in *m*-cresol at 30°C in an Ubbelohde viscometer with No. II capillary. To compare the course of the TPEEA polycondensation with that of typical polycondensations, the syntheses of poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and a copolyesterether (KPEE) were carried out in the above-described apparatus. Fig. 1

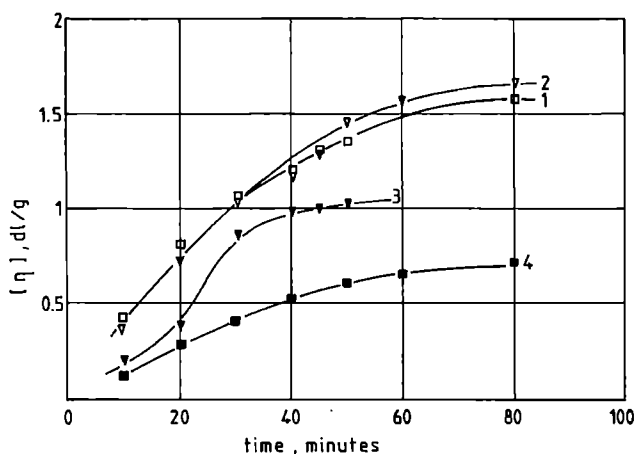


Fig. 1. Course of polycondensation, expressed as an increase in $[\eta]$ with time, for typical condensation polymers, in a 3.6 dm³ reactor; 1 — KPEE, 2 — KPEEA, 3 — PBT, 4 — PET

illustrates the advancement of these syntheses. As catalyst in the polycondensations of KPEE, PBT and KPEEA served $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and the temperature of the reaction was 260°C, whereas in the polycondensation of PET, Sb_2O_3 was used as a catalyst and the temperature of the reaction was 280°C. Figures 2, 3 and 4 illustrate the changes of LVN values during polycondensation reaction in the synthesis of KPEEA in relation to the mole-

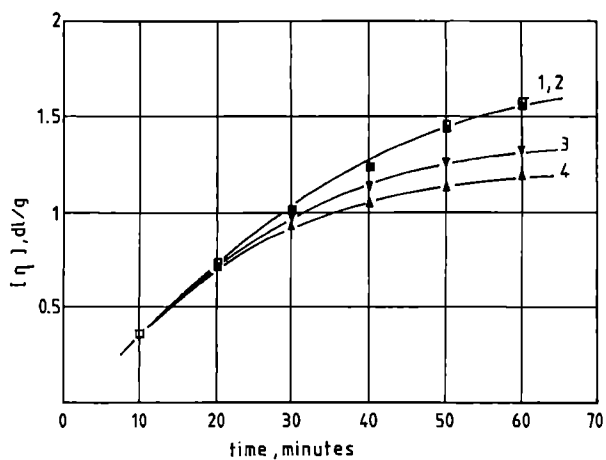


Fig. 2. The effect of molecular weight of OKL on the course of polycondensation to KPEEA with a constant content of PA (20 mass %) and with molecular weight of PTMO = 1000; 1 — PA-1500, 2 — PA-2000, 3 — PA-3000, 4 — PA-4000

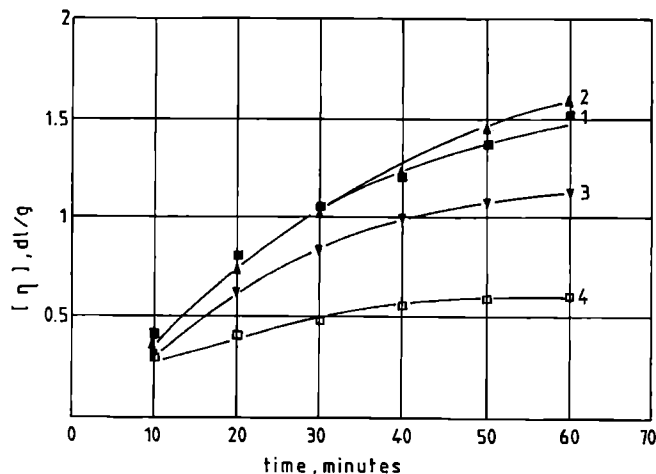


Fig. 3. The effect of PA content on the course of TPEEA polycondensations (molecular weight of OKL = 2000, molecular weight of PTMO = 1000); 1 — 0% PA, 2 — 20% PA, 3 — 30% PA, 4 — 40% PA

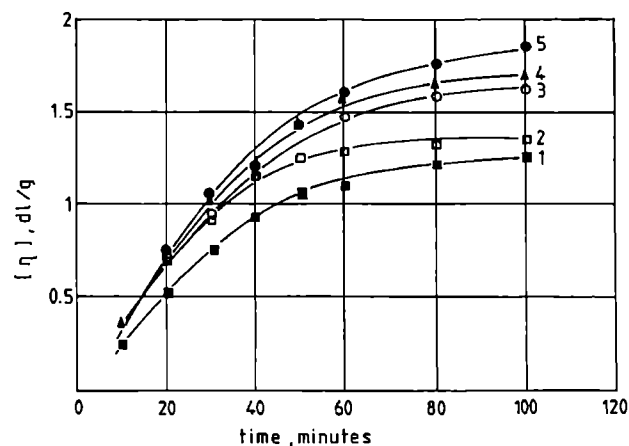


Fig. 4. The effect of PO4 content on the course of TPEEA polycondensation (molecular weight of OKL = 2000, content of PA block = 20 mass %, molecular weight of PTMO = 1000) 1 — 0% PO4, 2 — 10% PO4, 3 — 30% PO4, 4 — 40% PO4, 5 — 50% PO4, 6 — 60% PO4

cular weight and the mass fraction of α,ω -dicarboxylic oligocaprolactam as well as to the content of the oligo-oxytetramethylene (PO4) block. The most rapid as evident from the increase in LVN values *vs.* molecular weight, was the polycondensation of KPEEA with an OKL of molecular weight below 2000, with its content below 20 mass % and with the content of the soft oligoether block (PO4) above 40 mass %. It was not possible to prepare KPEEA with the content of PA-6 block above 30 mass % ($[\eta] < 0.9$, Fig. 3). This was probably due to the presence of a miscibility threshold of the reactants in the molten state. In table 2 there are compared the properties of a block copolyesterether produced in the Chemical Fibres Works „Elana” (trade name „Elitel 1”, implemented by the Technical University of

Table 2. PROPERTIES OF ELITEL 1 AND TPEEA RESINS

Properties	Elitel 1	TPEEA
Content of blocks with $T_g > 0^\circ\text{C}$, mass %	60	63
LVN, dl/g	1,25	1,41
Shore-D hardness	49	46
Specific gravity, g/cm ³	1,19	1,20
Tensile strength, MPa	26	29
Glass transition point, T_g (DSC), $^\circ\text{C}$	-60	-67
Melting point, $T_m^*)$ (DSC), $^\circ\text{C}$	203	205

*) Melting point of hard segment.

Szczecin) with those of the esteretheramide terpolymer containing 23 mass % of oligoamide blocks.

Conclusions

The possibility of synthesizing, under appropriate conditions and by the use of a suitable catalyst, a po-

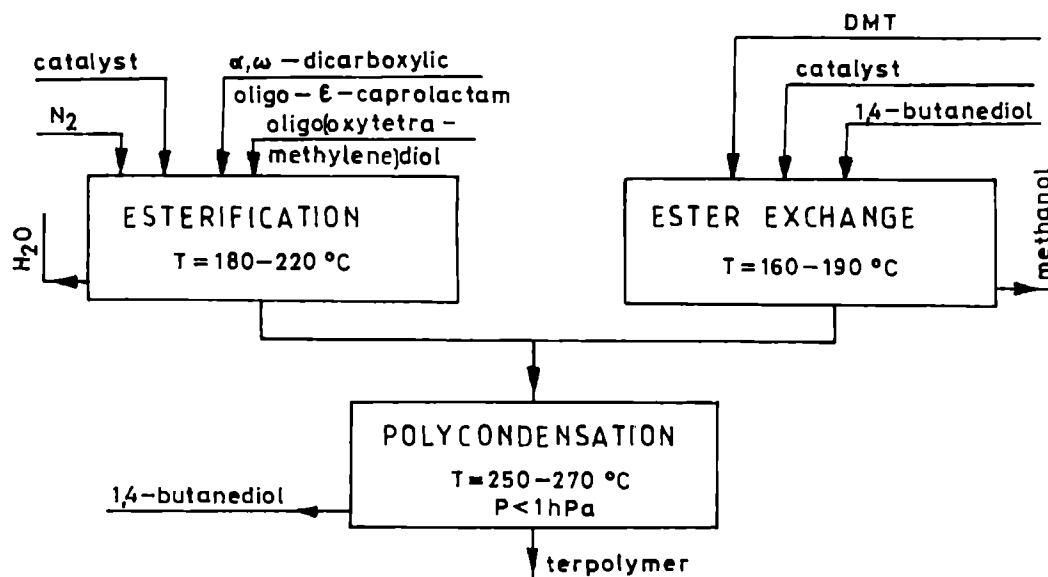
lymer comprising three immiscible blocks, namely the PO, PA and PE blocks, was demonstrated. No data dealing with this type of syntheses are hitherto reported in the literature.

It was found that PA-6 can be used in the synthesis of a polyesteretheramide terpolymer.

Light cream-coloured products were obtained with properties intermediate between those of copolyesterethers and those of copolyetheramides.

An analysis of the results indicated that both the course of the synthesis and the properties of the block TPEEA depend to a considerable degree on the chemical structure and on the length of the individual blocks. By changing the chemical structure and length of the blocks it is possible to prepare a TPEEA with desired properties.

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Flow sheet

REFERENCES

1. Ukielski R., Wojcikiewicz H.: *Int. Polym. Sci. Technol.* 1978, 5(10), T/61.
2. Ukielski R., Wojcikiewicz H.: *Int. Polym. Sci. Technol.* 1984, 11(4), T/61.
3. Ukielski R., Lembicz F.: *Polimery* 1985, 30, 105.
4. Ukielski R., Lembicz F.: *Makromol. Chem.* 1985, 186, 1670.
5. Ukielski R., Wojcikiewicz H.: *Polimery* 1988, 33, 9.
6. *Polish Patent* 108 711 (1978).
7. *Polish Patent* 137 158 (1983).
8. *Polish Patent* 150 278 (1990).
9. Ukielski R., Unpublished work, CPBR 3.4. tasks 125 and 136, reports of 1985–1989.
10. Słonecki J.: *Polimery* 1989, 34, 333.
11. *Polish Patent* 161 526 (1993).
12. XIth Scientific Conference on „Polymer Modification”, Communication — Chem—30, p. 214. Dusz-niki Zdrój, 26–30.09.1993.

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