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Properties of Copolyamido Esters Prepared by Anionic Copolymerization of ω-Dodecalactam, ε-Caprolactam, and ε-Caprolactone

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Abstract—The possibility of anionic copolymerization of ω-dodecalactam, ε-caprolactam, and ε-caprolactone in the presence of catalytic amounts of sodium caprolactamate and 2,4-toluene diisocyanate as activator was examined.

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The class of oxygen-containing heterocyclic compounds includes a wide range of substances: lactams, lactones, oxiranes, carbonates, peroxides, lactides, trioxanes, dioxolanes, etc. Of most practical interest are lactams and lactones, because their anionic polymerization via ring opening allows preparation of macromolecular compounds exhibiting a set of valuable characteristics and therefore finding wide practical use. At the same time, such materials have certain drawbacks. Polylactones have low flow point, low resistance to polar solvents, and poor strength; polylactams have low elasticity, low specific impact resilience, poor heat resistance, and high melting point limiting their reprocessing by plastic deformation in a melt.

By anionic copolymerization of lactams and lactones of various structures, it is possible to prepare copolyamido esters (CPAEs) combining rigid polyamide and flexible polyester components, which allows control over physicomechanical properties. Furthermore, both comonomers have similar structure and are capable of polymerization under similar conditions.

CPAEs based on ε-caprolactam (ε-CLM) and ε-caprolactone (ε-CLN) were prepared and studied in [1–3]. Their mechanical properties, as well as melting points, vary depending on copolymer composition: breaking stress, from 150 to 400 kg cm^{-2} and relative elongation at break, from 200 to 1100%. Copolymers of ω-dodecalactam (ω-DLM) and ε-CLN were studied only in [4], with sodium hydride used for generating catalytically active lactamate anions and ε-CLN itself acting as activator. The structures of the copolymers were examined by IR spectroscopy and X-ray phase analysis. The dependence of the melting points and heats of melting of the products on the content of the initial monomers was revealed. However, the mechanical properties of the CPAEs obtained were unsatisfactory because of low molecular weights.

Previously we prepared copolymers based on ω-DLM and ε-CLN with good physicomechanical properties [5]. However, the comonomers used in the process are relatively expensive and are imported. To make the products obtained cheaper, with their properties being preserved, we decided to use as a third comonomer ε-CLM, which is cheap and is commercially produced in Russia.

Thus, the goal of this study was preparation of terpolymers by anionic copolymerization of ω-DLM, ε-CLM, and ε-CLN in the presence of catalytic amounts of sodium caprolactamate and of 2,4-toluene diisocyanate as activator and elucidation of the effect exerted by the monomer ratio on the copolymer properties.

Table 1. Yield of copolyamido esters synthesized at various ratios of ω-dodecalactam, ε-caprolactam, and ε-caprolactone

Ratio, mol %			Yield, %
ω-DLM	ε-CLM	ε-CLN	
70	15	15	72
52	33	15	83
52	15	33	84
15	70	15	91
33	52	15	85
15	52	33	75
15	15	70	78
33	15	52	76
15	33	52	84
33	33	33	79

EXPERIMENTAL

ω-DLM and ε-CLM were recrystallized from absolute benzene, dried in a vacuum oven at 50°C, and stored in a desiccator under argon. ε-CLN was purified by vacuum distillation. Na-CLM was prepared as 25% solution in ε-caprolactam by reaction of the latter with sodium metal in the bulk at 110–115°C for 30 min. The product was stored in a desiccator over $CaCl_2$.

The copolymers were synthesized in an argon flow by the following procedure: 1 mol % Na-CLM was dissolved in a mixture of ε-CLM and ω-DLM at 180°C, after which the calculated amount of the comonomer (ε-CLN) and the activator (3 mol % 2,4-toluene diisocyanate) were added with continuous stirring. After the viscosity of the reaction mixture increased, afterpolymerization was performed for 120 min to decrease the amount of the unchanged monomer.

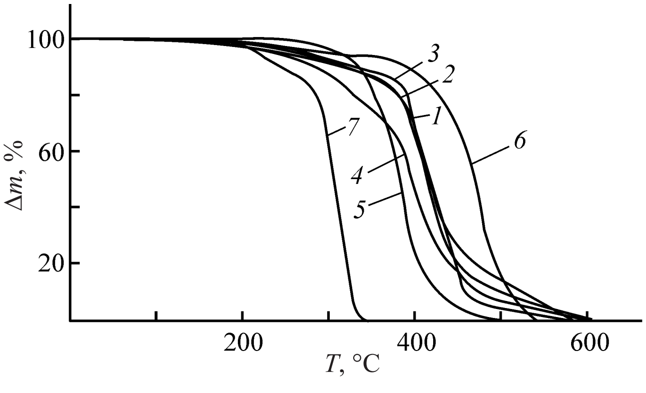

Fig. 1. TG curves of copolyamido esters prepared at various molar ratios ω-dodecalactam : ε-caprolactam : ε-caprolactone in the initial monomer mixture. ω-DLM: ε-CLM : ε-CLN: (*1*) 33 : 33 : 33, (*2*) 15 : 70 : 15, (*3*) 70 : 15 : 15, (*4*) 15 : 15 : 70, (*5*) 0 : 0 : 100, (*6*) 100 : 0 : 0, and (*7*) 0 : 100 : 0.

The resulting SPAEs were purified to remove unchanged monomers by extraction with acetone for 8 h.

The IR spectra were recorded on a Perkin–Elmer IR Fourier Spectrometer (PC-16 model). Thermogravimetric studies of the samples were performed with a Q-1500 derivatograph (MOM, Hungary) at a heating rate of 3 deg min^{-1}. Thermomechanical curves were taken on an installation for complex analysis. The spin–lattice relaxation time T_1 and the phase population were measured on a pulse NMR relaxometer with an operating frequency of 20 MHz. DSC studies were performed with a DSC 1 calorimeter (Mettler Toledo) at a heating rate of 5 deg min^{-1}. To determine the melt flow index (MFI), we used an IIRT capillary viscometer. The load weight and capillary diameter were 2.16 kg and 2.095 mm, respectively. The Shore hardness was measured with a portable electronic hardness gage with a TN-200 needle indenter. Samples for determination of physicomechanical characteristics were cut out from plates prepared by direct hot pressing at 60 to 230°C. Samples were tested no earlier than 24 h after the preparation and were conditioned at the test temperature for 4 h. In σ_t determination, the clamps of the tensile-testing machine were moved at a rate of 100 mm min^{-1}. The water absorption of the polymers was evaluated in percents as weight gain after swelling in distilled water for 24 h.

We prepared the terpolymers in 72 to 91% yield (Table 1). The terpolymers were pale yellow solids. The homo- and copolymers were insoluble in chloroform and acetone and partially soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

In the IR spectra of the CPAEs obtained, after extraction with acetone we found characteristic absorption bands of amides (Amide A 3300, Amide B 3070, Amide I 1640, Amide II 1540 cm^{-1}). The absorption band at 1700 cm^{-1} corresponds to C=O stretching vibrations in tertiary amides, and that at 1730 cm^{-1}, to stretching vibrations of the carbonyl group in aliphatic esters.

A TGA study of the CPAEs obtained (Fig. 1) showed that the weight loss was monotonic. This fact indirectly suggests that the copolymers rather than mixtures of homopolymers were obtained. This is also confirmed by

Table 2. Spin–lattice relaxation time T_1 of copolyamido esters

Ratio, mol %			T_1, μs	P_1, %	T_{2a}, μs	P_{2a}, %	T_{2b}, μs	P_{2b}, %
ω-DLM	ε-CLM	ε-CLN						
100	0	0	82.5	100	0.032	8.6	0.007	91.4
0	100	0	127.5	100	0.042	23.9	0.005	76.1
0	0	100	137.5	100	0.056	63.2	0.006	36.8
70	15	15	77.5	100	0.017	43.8	0.006	56.2
52	33	15	75.3	100	0.017	41.6	0.007	58.4
52	15	33	60.0	100	0.032	64.7	0.007	35.3
15	70	15	84.2	100	0.048	63.1	0.009	36.9
33	52	15	82.5	100	0.025	43.7	0.007	56.3
15	52	33	52.5	100	0.074	47.8	0.012	52.2
15	15	70	117.5	100	0.070	43.8	0.006	56.2
33	15	52	125.0	100	0.039	60.2	0.009	39.8
15	33	52	85.0	100	0.053	72.3	0.006	27.7
33	33	33	52.5	100	0.145	53.5	0.010	46.5

a pulse NMR examination of the CPAEs. All the samples are characterized by a single spin–lattice relaxation time T_1 (Table 2), and this time increases with an increase in the content of flexible lactone units in the polymer structure. Two relaxation times T_{2a} and T_{2b} suggest the presence in the copolymer of crystalline and amorphous phases.

The DSC curves have a single melting peak. In the case of CPAEs, this fact confirms the copolymer formation, in agreement with the previously made assumptions (Fig. 2). The DSC curves of the copolymers, compared to those of the homopolymers, have a broader interval of melting, which is due to their nonuniformity in molecular weight. This fact is apparently associated with the use of monomers differing in the reactivity and occurrence of various competing reactions in the course of copolymerization.

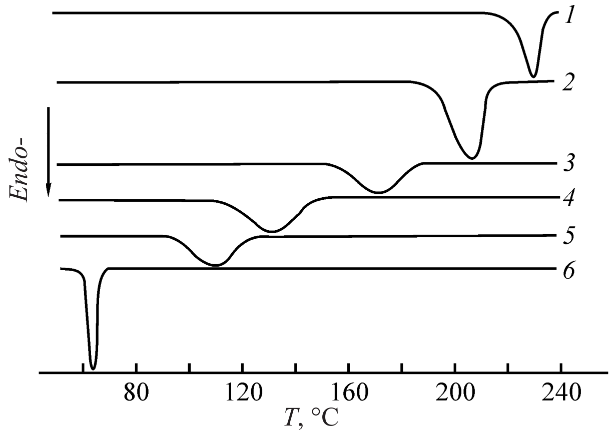

Fig. 2. DSC curves of copolyamido esters prepared at various molar ratios ω-dodecalactam : ε-caprolactam: ε-caprolactone in the initial monomer mixture. (*T*) Temperature. ω-DLM : ε-CLM : ε-CLN: (*1*) 100 : 0 : 0, (*2*) 0 : 100 : 0, (*3*) 15 : 70 : 15, (*4*) 70 : 15 : 15, (*5*) 33 : 33 : 33, and (*6*) 0 : 0 : 100.

The softening points determined from the thermomechanical curves varied in the range 80–180°C. The lowest values were observed with an excess of the polyester component (Fig. 3).

As the copolymers have different softening points, MFI was measured at different temperatures also. The

Table 3. Melt flow index of the terpolymers obtained

Ratio, mol %			MFI, g/10 min	*T*, °C
ω-DLM	ε-CLM	ε-CLN		
100	0	0	2.5	230
0	100	0	4.9	200
0	0	100	4.8	110
70	15	15	2.0	220
52	33	15	6.0	210
52	15	33	3.8	205
15	70	15	3.0	200
33	52	15	4.0	200
15	52	33	8.5	170
15	15	70	2.2	100
33	15	52	8.0	190
15	33	52	3.5	145
33	33	33	5.4	150

Table 4. Density and Shore hardness A of the copolyamido esters obtained

Ratio, mol %			Density, g cm^{-3}	Shore hardness A, rel. unit
ω-DLM	ε-CLM	ε-CLN		
100	0	0	0.91	95
0	0	100	1.11	97
0	100	0	1.00	97
70	15	15	0.97	97
52	33	15	1.03	94
52	15	33	1.00	95
15	70	15	1.01	96
33	52	15	1.06	92
15	52	33	1.06	92
15	15	70	1.07	96
33	15	52	1.10	95
15	33	52	1.04	96
33	33	33	1.15	96

MFI values for the copolymers (Table 3) are in the range 2–8.5 g/10 min in the temperature interval 100–220°C, whereas the MFI values of the lactam homopolymers are in the temperature range from 200 to 230°C. The results obtained, taking into account the rheological nomogram, show that all the copolymers can be processed into articles by pressure casting.

The densities of the copolymers varied from 0.97 to 1.15 g cm^{-3}, which is comparable with the densities of the corresponding polyamides and polyesters (Table 4). The Shore hardness of the copolymers varies from 92 to 98 and depends on the initial composition insignificantly (Table 4).

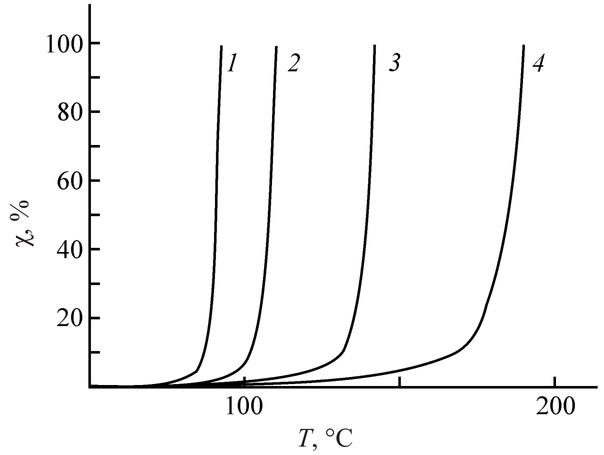

Fig. 3. Thermomechanical curves of copolyamido esters prepared at various molar ratios ω-dodecalactam : ε-caprolactam : ε-caprolactone in the initial monomer mixture. (χ) Deformation and (*T*) temperature. ω-DLM : ε-CLM : ε-CLN: (*1*) 15 : 15 : 70, (*2*) 33 : 33 : 33, (*3*) 70 : 15 : 15, and (*4*) 15 : 70 : 15.

To optimize the search for synergistic compositions, we used the simplex-lattice method of the experimental design and plotted the diagrams of the breaking stress, relative elongation, and water absorption for the CPAEs with the fractions of the three comonomers varying from 15 to 70 mol %.

Two areas of optimum properties can be revealed. The first area is centered at the initial monomer ratio ω-DLM : ε-CLM : ε-CLN = 52 : 24 : 24 and is characterized by the breaking stress in the range 40–47 MPa, relative elongation in the range 540–640%, and water absorption in the range 0.48–0.82%. With respect to the whole set of the properties, such copolymers considerably surpass the corresponding homopolymers. As for particular characteristics, lactams exhibit the highest breaking stress and poly-ε-CLN, the best elastic properties. These results are not surprising, as polyamide blocks have a more rigid-chain structure. It should be noted that one of major drawbacks of polyamides is relatively high water absorption, about 6% for ε-CLM, which negatively affects the properties of articles thereof.

However, from the viewpoint of the cost, of most interest is the second area with ε-CLM as major component. In this case, the breaking stress of CPAE (53 MPa) is similar to that of the strongest homopolymer, ω-DLM (50 MPa), the relative elongation (830%) appreciably exceeds that of homo-ε-CLN (625%), and the water absorption (3.5%) is almost two times lower than that of ε-CLM (5.7%).

CONCLUSIONS

(1) By performing anionic copolymerization of ω-dodecalactam, ε-caprolactam, and ε-caprolactone in the presence of catalytic amounts of sodium caprolactamate and of 2,4-toluene diisocyanate as activator, we prepared copolymeric products and examined them by thermogravimetric analysis, pulse NMR, and differential scanning calorimetry.

(2) Using the simplex-lattice method of experimental design, we suggested the optimum compositions of the copolyamido esters at which good physicomechanical characteristics are combined with relatively low water

absorption and with lower processing temperatures compared to lactam homopolymers.

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