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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis and Properties of Aliphatic Oligoamides Containing Methionine Fragment

E. V. Fomina, Yu. A. Kurskii, L. N. Beloded, and G. N. Chervyakova

Kargin Research Institute of Polymers, Federal State Unitary Enterprise, Dzerzhinsk, Nizhni Novgorod oblast, Russia

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Abstract—Oligoamides were prepared from dimerized fatty acid, hexamethylenediamine, and an amino acid (methionine). The effect of methionine on the course of polycondensation and properties of the reaction products was examined. New thermoplastic adhesive compounds based on these products were developed.

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Oligoamide products derived from dimerized fatty acid (DFA) and aliphatic diamines are widely used as base components of thermoplastic (hot-melt) adhesives [1-3].

The specific structural features and composition of the DFA used allow preparation of oligoamides exhibiting high adhesion to various materials, high shock resistance, flexibility, and resistance to water and oils [4, 5].

Introduction of various modifying agents (e.g., carbonyl compounds and dicarboxylic acids) into these oligoamides strongly affects the structure and properties of the products and, as a consequence, the characteristics of hot-melt adhesives based on them [6, 7].

Of particular interest in this respect is the modifying effect of methionine (α -amino- γ -methylthiobutyric acid), due to several reasons. First, a fairly bulky substituent, CH₃SCH₂CH₂, in the α -position of methionine should affect the physicochemical properties of the products [8–10]. At the same time, methionine plays an important role in biosynthesis processes, and introduction of its fragment into an oligoamide macromolecule may be a route to promising biodegradable materials, which would allow solution of environmental problems associated with the utilization of spent oligo- and polyamides [11, 12].

In this study we prepared a series of oligoamides differing in the content of methionine fragments and examined the specific features of polycondensation and the structure and properties of the products.

EXPERIMENTAL

As starting reagents we used methionine (Met) [GOST (State Standard) 23423–89], DFA of the PRI-POL 1017 brand (the Netherlands, CAS no. 61788-89-4), hexamethylenediamine (HMDA) [TU (Technical Specifications) 6-09-36–73), and wollastonite filler (NordKalk, Finland) FW-70, FW-325, and WIC-10 (mean particle diameter \leq 90, \leq 13, and \leq 4.5 µm, respectively).

The procedure for preparing oligo- and polyamides derived from DFA and aliphatic diamines is described in detail in [1, 2] and involves the polycondensation in a nitrogen atmosphere at $160-240^{\circ}$ C for 5-6 h without solvents and catalysts.

The synthesis of oligoamides modified with methionine is characterized by certain specific features associated with the fact that at $200-240^{\circ}$ C *D*-methionine melts with decomposition; also, the tendency of α -amino acids to cyclize on heating with the formation of 2,5-diketopiperazines [13, 14] should be taken into account.

Therefore, the joint polycondensation of DFA, HMDA, and methionine was performed under milder conditions, which allowed us to minimize the formation of diketopiperazines and avoid thermal decomposition of the amino acid molecules into low-molecular-weight products.

A reactor was charged with the required amounts of DFA and HMDA. The mixture was heated to 80– 100°C with stirring until a homogeneous mass was obtained. Then methionine was added, and the mixture was slowly (over a period of 40 min) heated with vigorous stirring to $160-165^{\circ}$ C, after which the water release started. Then the mixture was gradually (over a period of 7–8 h) heated to $195-200^{\circ}$ C. The final step was performed under the conditions ensuring efficient removal of water (133.32–666.60 Pa, 1–1.5 h, $140-190^{\circ}$ C). The product yield was 97.5–98.3%.

The modification of oligoamides with methionine can be represented by the scheme

$$(n + 1)H_2N-R-NH_2 + nHOOC-R'-COOH + nHOOC-CH-(CH_2)_2SCH_3 NH_2 \longrightarrow H_2N[RNHC(O)R'C(O)NHCHC(O)NH]_nRNH_2 (CH_2)_2SCH_3 + 3nH_2O,$$

where $R = (CH_2)_6$, $R' = C_{34}H_{62}$, n = 3-5.

The structure of the compounds prepared was studied by IR and NMR spectroscopy. The IR spectra were recorded on a Specord M80 spectrometer in the range 4000–700 cm⁻¹. The NMR spectra were measured on a Bruker DPX-200 spectrometer (operating frequency 200 MHz for ¹H and 50 MHz for ¹³C; solvent CDCl₃; reference tetramethylsilane).

The molecular-weight characteristics of the reaction products were studied by gel permeation chromatography (GPC) using a set of five Styrogel columns with pore diameters of 10^5 , 3×10^4 , 10^4 , 10^3 , and 250 Å (Waters). An R-403 differential refractometer (Waters) was used as detector; an LCD 2563 photometer (λ 254 nm) was additionally used; the eluent was tetrahydrofuran (THF). The chromatograph was calibrated with polystyrene references (polydispersity coefficient $\overline{M}_w/\overline{M}_n \leq 1.1$, molecular weight *M* in the range 2000– 100 000).

The amine numbers (AmN), acid numbers (AcN), and molecular weights (*M*) of the oligoamides were determined chemically from the amounts of terminal functional groups following the standard protocols [15]; the softening point T_s was determined by the ring-and-ball method (GOST 11506–73), and the shear strength of glue joints, according to GOST 14759–69.

The kinetics of the reaction of DFA, HMDA, and methionine was studied by measuring the amount of water distilled off during the reaction.

The kinetic curves (Fig. 1) show that the polycondensation of DFA with HMDA occurs more actively



Fig. 1. Amount *A* of water released in the polycondensation as a function of the reaction time τ . DFA : HMDA : Met ratio: (1) 0.40 : 0.50 : 0, (2) 0.40 : 0.50 : 0.10, (3) 0.40 : 0.50 : 0.25, and (4) 0.40 : 0.50 : 0.50.

in the absence of methionine: 70% of the theoretical amount of water is released during the first hour of the reaction; $\sim 90\%$, within 2 h; and $\sim 96\%$, within 3 h. Then, as the concentration of the functional groups of the starting compounds decreases, the reaction decelerates; it is complete in 6 h. In the reaction of DFA with HMDA and methionine, the rate of formation of the final product noticeably decreases with an increase in the methionine content. Addition of 0.1 molar equivalent of metionine causes the amount of water released during the first hour of the reaction to decrease to 60% of the theoretical amount; with 0.25 molar equivalent of methionine, this quantity decreases to 53%, and with 0.5 molar equivalent of methionine, to 45%. The total reaction time in the presence of methionine increases to 7-8 h.

Presumably, the mutual influence of the amino and carboxy groups in the methionine molecule and the presence of a bulky substituent, $CH_3SCH_2CH_2$, in the α -position relative to these groups lead to a certain deceleration of the polycondensation in the system DFA–HMDA–Met, compared to the Met-free system.

The polycondensation products are golden-yellow solids with a weak methionine odor; their properties are given in Table 1.

With an increase in the amount of Met added, the molecular weight of the polycondensation product gradually decreases. As compared to the product prepared from DFA and HMDA without methionine, *M* of the oligoamides containing methionine fragments is lower by a factor of 1.2–2.3. This fact may be due to structural features of methionine and to its capability to terminate the propagating oligomer chain. Correspondingly, the softening point decreases with increasing methionine makes the oligoamide structure irregular, causing an increase in the distance between

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Sample no.	Equivalent ratio of reactants			AmN	AcN		
	DFA	HMDA	Met	mg KOH/g	oligoamide		I _s , iC
1	0.40	0.50	_	20.5	1.5	5100	85
2	0.40	0.50	0.05	23.5	2.0	4400	80
3	0.40	0.50	0.10	30.3	2.3	3500	75
4	0.40	0.50	0.20	33.8	2.5	3100	68
5	0.40	0.50	0.25	40.8	3.9	2500	62
6	0.40	0.50	0.50	45.4	4.6	2200	56

Table 1. Properties of modified oligoamides prepared at different reactant ratios

the adjacent macromolecules and hence in the number of hydrogen bonds between the adjacent oligoamide chains; as a result, the softening point decreases [16].

To confirm the incorporation of methionine into the oligomer and determine how methionine is bonded with the oligomer, we examined the chemical structure of polycondensation products formed in the system DFA–HMDA–methionine by IR and NMR spectroscopy. The expected amide structure was confirmed by the characteristic amide vibrations [1]. However, we revealed no specific shift of the absorption bands under the influence of intra- and intermolecular interactions caused by the introduction of the amino acid containing a heteroatomic substituent in the α -position. Furthermore, assignment of S–C bands is complicated by their weak intensity, and identification of this fragment by IR spectroscopy is impossible.

The NMR spectra furnish more information. They convincingly confirm the incorporation of the amino acid into the oligoamide; the methionine fragments were detected in different parts of the oligomer chain:



Fig. 2. Gel chromatograms [(a) refractometric and (b) UV detector] of oligoamide samples. DFA : HMDA : Met ratio in the reaction system: (1) 0.40 : 0.50 : 0.25 and (2) $0.40 : 0.50 : 0.50 . (V_R)$ Relative retention volume and (*M*) molecular weight (polystyrene references).

both in the middle and on the ends. In the ¹H NMR spectrum, along with strong signals belonging to amide groups [1], we additionally detected signals of CH_3S protons at about 2.1 ppm, signals of the methine protons of the fragment

at 4.2 ppm, and signals at 4.6 ppm assignable to the methine protons of the fragment

$$HOC(O)$$

 $CH(CH_2)_2SCH_3$.
R'C(O)NH \checkmark

At the same time, we detected no expected signals of the methine protons of the fragment \sim RNHC(O) \cdot CH(NH₂)CH₂CH₂SCH₃ at 3.1 ppm. These signals, however, may be obscured by strong signals of the -CH₂C(O)NH- protons.

Examination of the molecular-weight distribution (MWD) of the compounds obtained involved certain problems due to low solubility in THF of highermolecular-weight samples containing from 0.05 to 0.2 molar equivalent of methionine. It is known that oligo- and polyamides are resistant to the majority of solvents used and dissolve only in substances containing strongly polar groups [17]. Therefore, we determined the molecular-weight parameters only for products containing 0.25 (Table 1, sample no. 5) and 0.50 (sample no. 6) molar equivalent of methionine, which had lower molecular weight (Table 1) and higher solubility in THF. This fact confirms the previous data [17] that the solubility of oligo- and polyamides in common solvents can be increased by performing the synthesis in the presence of components containing a sulfur heteroatom.

The gel chromatograms of the reaction products obtained from DFA, HMDA, and methionine are shown in Fig. 2. It should be noted that calculation of the molecular weights from the polystyrene calibration

Sample	Chemical	GPC (refractometric detector)			
no.	method, M_n	\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$	
5 6	2500 2200	2000 1500	7800 5400	3.9 3.6	

Table 2. Molecular parameters of sample nos. 5 and 6

does not give true molecular weights but allows adequate comparison of the MWDs of different samples of similar nature [18].

The chromatographic patterns show that the fractional composition of the samples obtained is nonuniform, with the prevalence of low-molecular-weight and oligomeric fractions; the MWD curves are essentially bimodal. The mean molecular weights M are $600 < M < 40\,000$ for sample no. 5 and $600 < M < 32\,000$ for sample no. 6.

The MWD data for methionine-containing oligoamides are given in Table 2.

A comparative analysis of the molecular weights of methionine-containing oligoamides shows that the number-average molecular weights obtained using various methods are in reasonable agreement. The GPC examination confirmes a decrease in M of the oligomer with an increase in the methionine content.

Methionine-modified oligoamides were used for the development of new thermoplastic adhesive formulations. Along with single-component hot-melt adhesives consisting of the base thermoplastic only, we tested a series of filled adhesives. Here we report the results obtained with wollastonite, one of the most promising fillers. Table 3 shows that introduction of wollastonite considerably expands the working temperature range of adhesive formulations, shortens the curing time, enhances the shear strength of the glue joint, and decreases the cost of the adhesive.

It should be noted that such an effect of wollastonite on the properties of adhesive formulations is determined by a characteristic needle-like shape of its crystals and by the specific chemical composition. Owing to the active surface of the particles, this filler is capable of hydrogen bonding with oligoamide molecules; an important factor is the dispersity of the wollastonite [19, 20]. Our results show that the best physicomechanical and processing characteristics are exhibited by filled hot-melt adhesives containing 20 or 50 wt % wollastonite; the strongest effect is attained with 50 wt % wollastonite WIC-10.

CONCLUSIONS

(1) Addition of methionine to the reaction mixture in the synthesis of oligoamides from dimerized fatty acid and hexamethylenediamine decelerates by a factor of 1.5, on the average, the polycondensation and formation of the final product.

(2) With an increase in the relative amount of methionine, the molecular weight of the product decreases by a factor of 1.2-2.3, and the softening point, by $5-29^{\circ}$ C.

Table 3. Composition and properties of hot-melt adhesives based on methionine-modified oligoamide (DFA : HMDA : Met = 0.40 : 0.50 : 0.25)

Component	, wt %	T _s	T _{appl}	Curing time s	Shear strength
oligoamide	wollastonite	°C		Curing time, s	(Al–Al), MPa
100	FW-70:	62	110–115	4	5.0
90	10	66	110-120	3	5.4
80	20	75	120-130	3	6.0
50	50	89	130-140	2	7.3
	FW-325:				
90	10	65	110-120	3	5.3
80	20	74	120-130	3	5.8
50	50	85	130-140	2	6.5
	WIC-10:				
90	10	69	115-120	3	5.6
80	20	78	125-135	3	7.2
50	50	89	140–145	2	8.0

(3) A series of wollastonite-filled thermoplastic adhesive formulations based on methionine-containing oligoamides were developed.

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