

CHARACTERIZATION OF POLYMERIC MATERIALS BASE ON THE OLYGOMERS WITH TERMINAL FUNCTIONAL GROUPS

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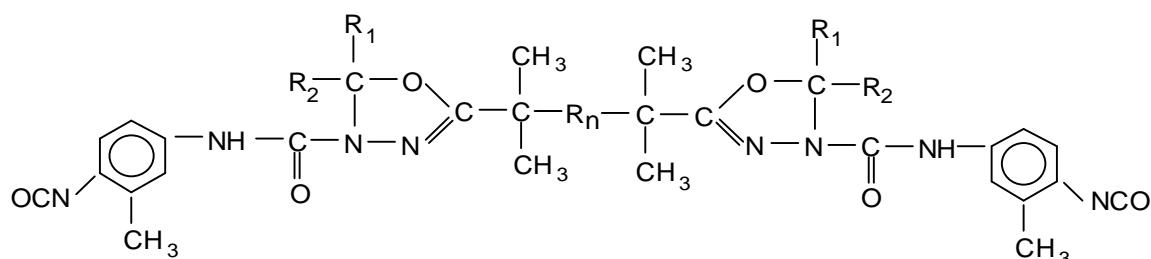
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Liquid oligomer systems are characterized by a certain type of the intermolecular organization which influences laws of formation and polymer properties. One of the important factors defining supramolecular structure of polymer is the presence of polar functional groups able to form molecular associates of different types. The influences of functional end groups oligomers of different chemical nature on laws of synthesis and properties of the new obtained polymeric materials have been studied.

Macrodiisocyanates on the base of oligodienediacylhydrazones of aliphatic ketones and diisocyanates obtained at the molar ratio of 1:2,1, accordingly, in the solution of a ester, at 393-403 K, during 0,25-1 hours. It was established that during reagents interaction there is the reaction of cyclization of acylhydrazone groups with the formation of oligoisoprenoksadiazolinilcarbamate diisocyanates (OIODCI), containing 1,3,4-oxadiazoline cycles, with the following structure :



where: R: -C₄H₆-, -C₅H₈-; R_{1,2}: -Alk; n = 50-60.

Interaction of oligodienediacylhydrazones with diisocyanate has been finished at reduction on 50 % of the intensity of absorption band in the IR-spectrum, characteristic for N=C=O groups, in the range of 2240–2270 cm⁻¹ (Figure 1).

The possibility of incorporation of various functional end groups into oligomers, which may interact with a broad range of reagents, permits to develop oligomeric compositions with controlled conditions of curing and cured polymers with tailored properties.

The isocyanate-containing forepolymers were cured with di- and polyfunctional agents with active hydrogen atoms. The compositions were prepared directly before using. The gel time was determined by the nature of a curing agent and changed from 15-60 min. to 8-30 h. The study of the forepolymer curing showed that the best technological and mechanical characteristics of polymeric materials are achieved using aromatic diamines as chain extenders. So, by curing an isocyanate-containing forepolymer prepared from liquid rubber and 3,3-dichloro-4,4-diaminediphenylmethane in organic solvent, which does not have in its structure active hydrogen atoms, e. g. methylethylketone, a series of polymeric materials were obtained and they are characterized by high physico-chemical properties, depending on the ratio of soft (forming on the base of diene chain) and hard (forming on the base of diisocyanate and a chain extender) blocks.

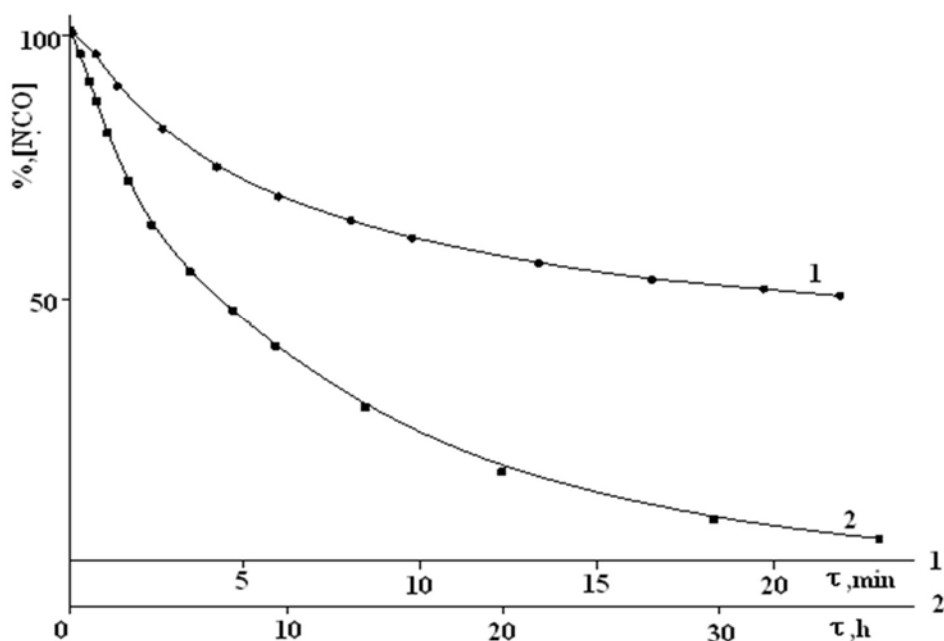


Figure 1. Kinetic laws of formation of OIODCI (1) and polyisoprenoksadiazolinil-carbamate (PIODC) (2)

Decreasing an elastic block length of these polymers leads to increasing their hardness and strength. In Table 1 the properties of linear polymers on the base of oligodienedihyrazones of various molecular weights and 50% solution of 3,3-dichloro-4,4-diaminediphenylmethane in methylethylketone are presented.

Table 1

The properties of polymers on the base of oligodienedihyrazides of various molecular weight

Molecular weight	Shore A hardness	Tensile strength, MPa	Tensile elongation, %	Residual elongation, %
1350-2000	85-95	20-25	200-400	0-4
2350-3000	69-85	12-20	300-400	0-8
3350-4480	52-69	6-12	350-500	2-10

The hydrophobicity of diene blocks in a polymer chain explains the fact that elastomers obtained have swelling as low as 10-100 times compared with urethane elastomers based on polyethers.

The resistance of elastomers to the influence of acid and alkali solutions of different concentrations was determined by the comparison of physico-mechanical properties (tensile strength and tensile elongation) of the obtained polymers before and after their submission to the corrosive environment. The investigation was carried out at the temperature $22 \pm 2^{\circ}\text{C}$ for 1000 h.

The specimens were considered to be stable if they saved up to 80% of mentioned properties. The results of the polydieneoxadiazolinylcarbamates resistance to the influence of corrosive media are shown in Table 2.

The changes of the stability coefficient are connected with changing of the oxadiazolinylcarbamate group (formed by the interaction of acylhydrazones with isocyanates) to acylsemicarbazide under the influence of liquid corrosive media.

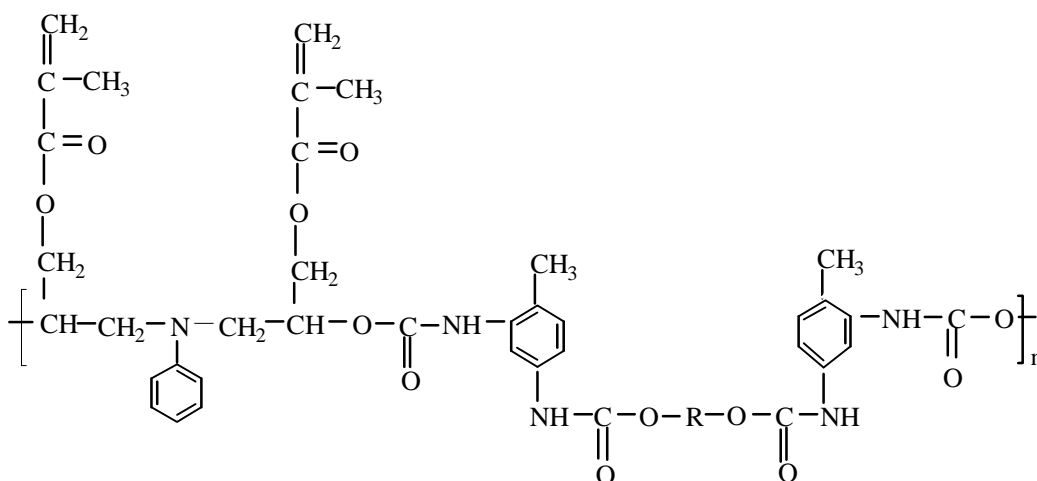
Resistance of the polymers based on oligodienedihydrazone, 2,4-TDI and 3,3-dichloro-4,4-diaminodiphenylmethane (reagent ratio 1:2:1) to the influence of corrosive mediums

Test medium	Concentration, %	Swelling degree, %
H ₂ O	-	0,07
HNO ₃	30	2,99
H ₂ SO ₄	50	-0,39
H ₃ PO ₄	50	-1,40
HCl	10	-0,32
HF	30	2,22

It is of interest to examine block copolymers in which unsaturated bonds occur in hard blocks (containing urethane, urea, phenyl, semicarbazide, and other polar groups) alternating with soft blocks (containing polyester, polydiene groups). The incompatibility of soft and hard blocks with different chemical compositions gives rise to a stable microphase separation; as a result, domains consisting of hard blocks are formed in the soft matrix. These domains serve as junctions of the three-dimensional physical network of the copoly(urethane) block largely via hydrogen bonds that are tens of times less strong than chemical bonds. Therefore, a certain mobility is preserved in stiff blocks. This situation makes it possible to form additional chemical bonds under certain conditions upon heating or irradiation of block copoly(urethanes).

Synthesis of photocured elastomeric materials was carried out in two stages: by interaction of functional end groups of the initial oligomers with spacers containing nonsaturated groups, and then photopolymerization of these groups. In this way, the soft elastic material is formed in the first stage, it can be molded in certain forms and sizes, and then increase of durability properties during the photocuring stage.

On the basis of oligodieneurethane diisocyanates or oligoetherurethane diisocyanates and dimethacrylate (DMA) yields in poly(ester urethane diacrylate)s (PEUA) or poly(diene urethane diacrylate)s (PDUA) and poly(dieneoksadiazolinil-carbamate urethane diacrylate)s (PDODCA) with the following structure:



R: -CH₂CH₂O-, -C₄H₆-, -C₅H₈-; n = 45-60.

The Table 3 shows the properties of the initial PEUA film, the film exposed to UV light (with benzoin isobutyl ester as initiator) and the film that was initially uniaxially stretched and

then irradiated. The irradiated films exhibit a higher onset temperature of degradation, better strength, and, accordingly, lower elongation. This effect is associated with the formation of chemical bonds that appear in the hard block of the polymer upon UV irradiation. The properties of uniaxially stretched and not stretched irradiated films are also different.

Table 3

Properties poly(ester urethane diacrylate) before and after

Film	Solubility in DMF	Onset temperature of degradation, °C	Tensile strength, MPa	Elongation at break, %
Starting	Soluble	200	2-5	500-700
Irradiated	Insoluble	230	8-12	200-250
Stretched by 100% and then irradiated	Insoluble	260	15-20	80-100

This situation may be explained by the orientation of functional groups in the hard block. As a result, additional physical bonds develop in the polymer and its supramolecular structure changes under mechanical stress (stretching) and irradiation.

The glass temperatures of flexible oligodiene blocks ($T_{g1} = 231$ K for PDODCA and $T_{g1} = 235$ K for PDUA) are rather distinctive from glass temperatures of oligoisoprenes ($T_{g1} = 212-215$ K) (Table 4).

Table 4

Thermodynamic characteristics of the PDUA and PDODC

Samples	$T_{g,1}$ K	$\Delta C_{p,1}$ J/(g·K)	$T_{g,2}$ K	$\Delta C_{p,2}$ J/(g·K)
PDUA	235	0,22	340	0,50
UV-irradiated PDUA	235	0,20	327	0,41
PDODCA	231	0,25	338	0,39
UV-irradiated PDODCA	231	0,23	328	0,59

Magnitude of $T_{g,2}$ for PDUA slightly decrease against $T_{g,2}$ PDODCA but magnitude of $T_{g,2}$ for UV-irradiated PDUA increase against $T_{g,2}$ UV-irradiated PDODCA which could be explained by the presence of different network of hydrogen bonds with participation of urethane metacrylates groups and oxadiazoline carbamate urethane metacrylates groups. As level of hydrogen bondings in PDODCA is higher than in PDUA, restricted mobility in the hard blocks in the first case is more considerable that proves to be true lower degree of transformation metacrylates tied in the hard block. Accordingly, it leads to difference in properties of these polymers before and after photostructuring.

Thus, a series of polymer materials was developed on the base of the reactive oligomers by a progressive method without solvents through a stage of isocyanate forepolymer synthesis. The physico-mechanical properties and abrasive-corrosive resistance of these polymeric materials may be improved, if necessary, during the process of exploitation in corrosive media.