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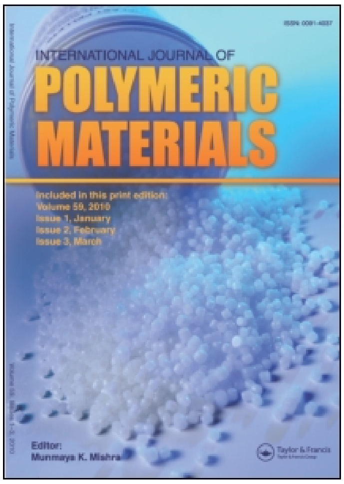

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L. A. Sukhareva[a]; E. G. Rozantzev[a]
[a] Institute of Biotechnology, Moscow, Russia

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The Influence of Mesomorphic State on the Durability of Polymer Coatings

L. A. SUKHAREVA and E. G. ROZANTZEV

Institute of Biotechnology, 33, Talalikhin Street, Moscow 109029, Russia

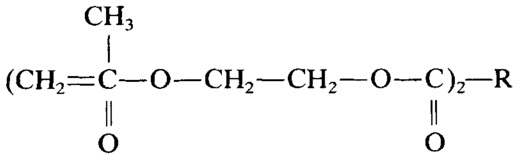
The laws governing the destruction of polymer coatings during their use are partly defined by the fact that the rate and other specific features of their destruction are influenced by internal stresses occurring as a result of incomplete relaxation processes due to peculiarities of structure formation.[1] This paper deals with an investigation carried out with the help of the NMR method of higher resolution, electron microscopy and physicochemical methods to study the effect of the oligomeric block structure, length and flexibility of a number of oligoester acrylates on peculiarities of oligomer structure formation as well as coatings structure and properties and their durability in the conditions of aging under ultraviolet radiation. It's been shown that coatings set through the intermediacy of mesomorphic structure formation have increased durability of 2–2.5 times, during aging under ultraviolet light radiation. Of all the studied systems those with a globular structure tend to have the lowest durability.

KEY WORDS Coatings, durability, mesogenes

Using various physicochemical methods it has been established,[2,3] that coatings destruction is accompanied by complex structure transformations at the molecular and supermolecular levels which are different in different film layers due to the presence of defects and layer to layer heterogeneity of the structure. Thus internal stresses can both increase and decrease the energy required for activating the destruction processes.

By means of the ESR method there has been found[4] an increase in the flexibility of local structural elements in the amorphous regions and defects of the polymer crystal lattice exposed to aggressive media. This brings about a lowering of internal stresses. It makes it possible to use kinetic changes of internal stresses in the aging process to evaluate the rate of destruction and to regard them as criteria for coatings durability. The object under study has been a number of oligocarbonate methacrylates with the same active functional groups (double bonds, carbonate groups) taking part in space network formation and adhesive interaction with the substrate but different in the oligomeric block length and flexibility and hence in the macromolecular conformation and the level of supermolecular organization in both the liquid phases and the coatings.

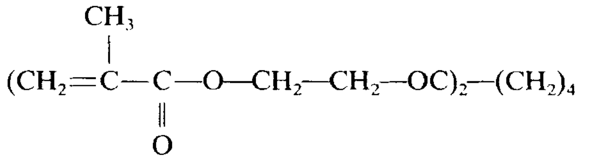
The general formula of oligocarbonate methacrylates is the following[5]:



$$(CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}}-O-CH_2-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{C})_2-R$$

where R: $—(CH_2)_2$-α,ωbis (methacryl oxyethylene carbonate) ethylene glycol (OCEM); $—(CH_2)_3$-α,ωbis (methacryl oxylenecarbonate) propandiole (OCPM); $—(CH_2)_4$-α,ωbis (methacryloxylenecarbonate) butylene glycol (OCBM); $—(CH_2)_6$-α,ωbis (methacryl oxylenecarbonate hexamethylene glycol (OCHM); $—(CH_2—O—CH_2)_2$-α,ωbis (methacryl oxyethylene) carbonate diethylene glycol (OCDM).

For comparison, a study has also been made of an analog of OCEM having a similar chain structure but containing ester groups instead of carbonate groups which has the following formula:



$$(CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}—\underset{\underset{\displaystyle O}{\|}}{C}—O—CH_2—CH_2—OC)_2—(CH_2)_4$$

α,ω,bis (methacryl oxycarbonate) adipinate (MEA).

Table I shows oligomer physical constants. The OCHM melting temperature is 38°C. The oligomer glass-transition temperature was calculated by the maximum position of the oligomer thermal conductivity coefficient on the curves of temperature dependence. The introduction of an oxygen bridge between two methylene groups into the oligomeric block having the same chemical composition allowed a great increase in the chain flexibility. This is supported by the data on the glass-transition temperature of the analogous oligomers (OCBM and OCDM) which have a similar composition.

The effect of the oligomeric block structure of oligoester acrylates on the coating's durability has been studied by investigating the characterictics of changes in the internal stresses and the thermal conductivity coefficient versus the aging period. The coatings were exposed to ultraviolet radiation, using PRK-2 lamp. Total radiant intensity amounted to 69.8 wt/m^2, while ultraviolet radiation intensity came to 56.5 wt/m^2. The samples were held at a distance of 200 mm from the source of radiation, their surface temperature being 36–38°C which is much lower than the destruction temperature, 230–300°C of the studied oligoester acrylates.

By means of the ESR method, infrared spectroelectron microscopy and physico-

TABLE I

The oligomer physical constants

Oligomer	Molecular mass		Density, 10^3, kg/m^3	Viscosity, 10^{-3}, cP	Oligomeric block length, nm	T_g, °C
	Found	Calculated				
OCEM	382	374	1.209	272	1.94	−65
OCPM	380	388	1.194	135	2.07	−75
OCBM	410	402	1.179	170	2.19	−75
OCHM	440	430	1.100	hard	2.45	−77
OCDM	427	419	1.208	309	2.30	−81
MEA	397	370	1.135	220	2.09	−77

mechanical studies it has been previously established[1] for different film-forming types of coatings that a sharp decrease of internal stresses and a build-up of the thermal conductivity coefficient at a certain stage of aging are caused by destruction processes at the molecular and supermolecular levels. Figure 1 shows the kinetics of changes of internal stresses in the aging process of oligomer coatings that differ in length, flexibility and chemical composition of the oligomeric block, under ultraviolet radiation. A significant decrease of internal stresses caused by the destruction processes is seen to begin after 350–400 hours of radiation for oligomer coatings with shorter and more rigid oligomeric blocks. For OCDM coatings this process starts after 150–200 hours.

Similar trends are observed for the kinetics of changes in the thermal conductivity coefficient during aging under ultraviolet radiation for the coatings based on the oligomers under study (Figure 2). While studying the thermal conductivity coefficient the coatings resistance to aging was evaluated by the horizontal portion of the kinetics curve. The foregoing data testify to a good accord of the results of the durability studies carried out by means of the two different methods.

A pronounced effect of the oligomeric block length and flexibility on the coating's

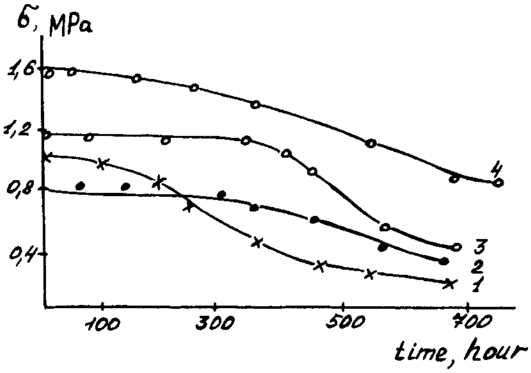


FIGURE 1 Changes in interal stresses during the aging process of the coatings.

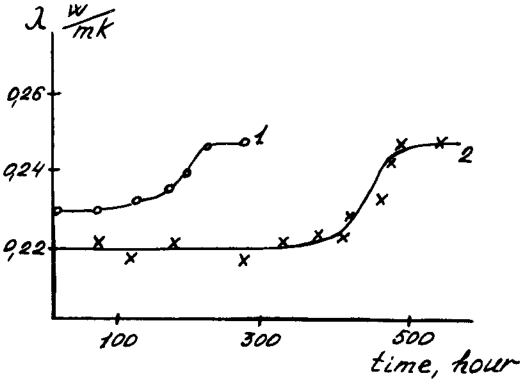


FIGURE 2 Changes in the thermal conductivity coefficient depending on the aging period for the coatings from OCDM (1) and OCFM (2).

durability is due to the level of supermolecular organization in the initial oligomers and the coatings formed on their basis. The oligomer structure formation, studied by means of the NMR method of higher resolution, made it possible to establish the associated formation mechanism by comparing the data on the dependence of molecular mobility of the end and carcass groups of the oligomeric blocks of the oligocarbonate methacrylates OCEM and OCDM versus temperature.[6] The uncoiled conformation has been shown to be developed while forming associates from the OCEM molecules. This is supported by data on the loss of mobility of the end and carcass groups of the oligomeric block simultaneously with an oligomer temperature decrease. The uncoiled conformation of molecules with short and rigid oligomeric blocks appears to cause formation of anisodiametric structural elements similar to the mesophases of the non-flattening type. A considerable flexibility of OCDM molecules results in associations formed from coiled globular type molecules.

The effect of molecular conformation on the peculiarities of structure formation is also confirmed by the infrared spectra of the oligocarbonate methacrylates under study. Thus, according to the intensity of the absorption bands in the region of about 1650 cm^{-1}, characteristic of the valence vibrations of double bonds conjugated with a carbonyl group, and to the out-of-plane deformational vibrations of the hydrogen atom in methylene groups, the oligomers under study can be arranged in the series of OCEM > OCBM > OCHM > OCDM. With the structure of the oligomeric block being similar, the greatest number of bonds and their highest spectra in the regions of the vibration frequency typical of ester bonds and methylene groups is observed for the coatings based on OCEM and OCBM as compared to OCDM.

These data are in accord with the results of a study carried out by other methods on the increase of intermolecular interaction between structural elements with uncoiled molecular conformation and on a marked effect of associated structure on the level of supermolecular organization in crosslinked polymers and their properties. By means of electron microscopy it has been established that anisodiametric structural elements of the non-flattening type remain in the coatings formed from the oligomers OCEM and OCBM as distinct from the other oligomers under study forming network polymers with a globular structure.

The influence of the length and flexibility of the oligomeric block of oligoester acrylates with terminal reactive groups on polymerization kinetics in a thin layer has been studied by means of infrared spectroscopy.

Figure 3 gives data on the depth of conversion of double bonds upon oligomer polymerization during hardening of coatings at 80°C in the presence of the redox system of cumene peroxide and B-accelerator. Figure 3 shows that polymerization of oligoester acrylates with a regular alternation of polar groups in the oligomeric block proceeds quickly and to a high level of conversion. The highest rate of double bond consumption is observed for the oligomer OCEM having the shortest and the most rigid oligomeric blocks in the series of oligocarbonate methacrylates. The rate of polymerization decreases with the increase of the length and flexibility of the oligomeric block. It is also of interest to note a different character of kinetic curves upon the OCHM polymerization as distinct from the other oligomers, in

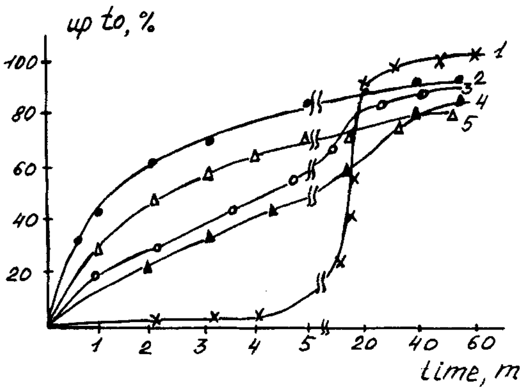


FIGURE 3 The depth of conversion of double bonds upon polymerization of the oligomers OCHM (1), OCEM (2), OCBM (3), MEA (4), OCDM (5) during hardening of coatings.

TABLE II

Physicomechanical properties of coatings from oligoester acrylates

Oligomer	Tensile strength, MPa	Ultimate elongation, %	Elasticity modulus, 10^{-3}, MPa	The degree of lacing, 10^{21}, units/cm^3	Adhesion strength, MPa	Internal stress, MPa
POCEM	76	2.6	3.9	2.0	7.0	0.7
POCPM	68	4.4	2.5	1.6	4.0	1.8
POCBM	68	4.7	2.5	1.7	9.0	1.0
POCDM	61	4.6	3.0	1.5	1.4	1.3
POCHM	60	4.8	2.3	1.6	3.0	2.0
PMEA	58	5.6	2.1	1.6	2.8	1.6

particular, the existence of an induction period due to crystal phase melting. Similar trends for the oligomers under study are established when evaluating a change in the absorption band intensity for the groups participating in the intermolecular interaction and manifesting themselves in the region of 1180 cm^{-1} characteristic of ester groups. It is interesting to demonstrate that the rate of a coating's hardening is greatly reduced and the polymerization process proceeds to the conversion of 80% in 2 hours for the OCPM oligomer having a short length of the oligomeric block but containing an odd number of methylene groups.

The IR spectra for this oligomer differ from the spectra for the oligocarbonate methacrylates having an even number of methylene groups by the presence of absorption band in the region of 1800–1810 cm^{-1} characteristic of carbonyl group overtones. It may point to the fact that the molecules of the OCPM oligomer with an odd number of methylene groups have a different configuration, their functional groups being in cis-position while trans-position is observed for them when having an even number of methylene groups.

Specific features of structure formation in the formation of the coating greatly affects their physicomechanical properties (Table II).

As is seen from Table II, oligomers with an ordered molecular structure while curing form crosslinked polymers with a high degree of lacing and good strain-strength indices. Yet, the level of supramolecular organization of associations and structural elements formed in their hardening has a marked affect on the coating's adhesion strength with the value of internal stresses changing as much as 3–5 times depending on these factors. The OCEM and OCBM based coatings have the highest adhesion strength and the lowest internal stresses for which anisodiametric structural elements from uncoiled molecules are observed providing for the most beneficial kinetic order for the participation of active functional groups in adhesion and cohesion interaction. The MEA-based coatings which are different from the OCBM oligocarbonate methacrylate, having ester groups instead of carbonate groups, tend to have much lower adhesion strength, the difference in the oligomeric block length being small. The adhesion strength is seen to be the lowest for the OCDM-based coatings characterized by a nonuniform globular structure. Accordingly, these coatings exhibit more than 2 times lower durability when exposed to ultraviolet radiation. The OCDM-based coatings having an odd number of methylene groups differ from their analogs having a similar length of the oligomeric block but containing an even number of these groups by adhesion strength as much as 2 times lower too, hence their durability is also lower.

Matching maintenance properties to the coatings structure one may safely come to the conclusion that the coatings having supramolecular structure and anisodiametric morphology similar to non-flattening mesophases and exhibiting superior properties and enhanced durability. Such structures are formed from the molecules of the oligomers having an even number of methylene groups and an optimum length and flexibility of the oligomeric block.

References

1. L. A. Sukhareva, Durability of polymer coatings, Moscow, *Chemistry*, (1984) p. 240.
2. P. I. Zubov and L. A. Sukhareva, Structure and properties of polymer coatings, Moscow, *Chemistry*, (1982) p. 256.
3. Ia. V. Moiseev and G. E. Zaikov, Chemical resistance of polymers to aggressive media, Moscow, *Chemistry*, (1979) p. 288.
4. A. M. Shapiro, V. V. Stryukov, B. A. Rozenberg, G. Z. Grigoryan and E. G. Rozantzev, High molecular compounds, **B4**, 265–267 (1975).
5. A. A. Berlin, L. A. Sukhareva and T. I. Kefelial, High-molecular compounds, 18, **A2**, 432–438 (1978).
6. L. A. Sukhareva, Polyester coatings, Moscow, *Chemistry*, (1978) p. 197.