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Investigation of the Structure and Properties of Crosslinked Polymers Based on Oligocarbonate Methacrylates in Film Formation

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ABSTRACT

The effect of structure and flexibility of an oligomeric block of oligocarbonate methacrylates (OCM) as well as of various modifiers on the coating formation, the structure, and properties of crosslinked polymers formed under conditions of adhesive interaction has been studied. Reactivity and conversion of OCM during polymerization increase in coatings formed from oligomers with short and rigid blocks, capable of forming on the substrate a network from the ordered anisodiametric structural elements with high adhesive properties, as distinct from the globular structures appearing in the formation of the network from the oligomers with more flexible blocks. The tendencies observed have been explained with the aid of a mechanism of network formation relating the morphology of the resultant crosslinked polymers to the flexibility (conformation) of the chains of the branched polymer obtained in the initial stage of polymerization and representing a matrix of the corresponding crosslinked structures. The mode of action of modifiers is markedly dependent on the nature and flexibility of the oligomeric block.

INTRODUCTION

The concepts of microheterogeneous structure of crosslinked polymers have been supported by the studies of the three-dimensional polymerization kinetics of oligoester acrylates and their analogs [1], and by investigation of the mechanism of the formation of rubber networks and oligoester acrylate copolymers [2], polyurethanes [3, 4], and polymers based on unsaturated oligoesters with a statistical distribution of double bonds [5-7].

At the same time, the effect of formation of supramolecular structure in liquid oligoester acrylates (OEA) on the rate of the three-dimensional polymerization, structure, and properties of the corresponding crosslinked polymers has been established [8].

To produce an ordered supramolecular structure, different methods have been used to modify the oligomers by surfactants [9], thixotropic additives [10], rigid-chain polymers [11], and organic silicon compounds with a regular alternation of active and inactive groups [12].

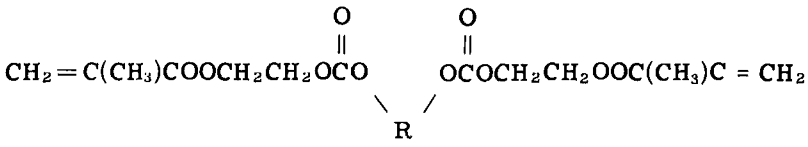
However, up to now only limited studies of the specific features of oligomer polymerization in a thin layer and of the structures and properties of crosslinked polymers appearing as a result of the adhesive interaction have been carried out.

Such information is extremely needed for the development of ideas on the mechanism, structure, and properties of crosslinked polymers which serve as the basis for coatings, binders, and filled plastics.

This paper deals with studies of the effect of the flexibility of unsaturated oligoester oligomeric blocks with a regular structure on the kinetics of their polymerization in a thin layer upon contact with a glass substrate, on the internal stresses, structure, adhesion, and endurance of the resultant coatings. The flexibility of the oligomeric block was varied by introducing into the chain functional groups of various types which modifying the potential rotary barrier and introducing structure-forming polymeric additives with a conjugated system (PCS).

EXPERIMENTAL

To solve the problem given above, we investigated individual polymerizable oligomers with terminal reactive groups and an oligomeric block containing regularly alternating polar groups. Such compounds include the oligocarbonate methacrylates described recently in the literature [13] and having the general formula I



$$CH_2{=}C(CH_3)COOCH_2CH_2O\overset{\overset{O}{\|}}{C}O\underset{R}{\diagdown\;\diagup}O\overset{\overset{O}{\|}}{C}OCH_2CH_2OOC(CH_3)C=CH_2$$

I

where R = $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, or $-CH_2CH_2OCH_2CH_2-$.

Of these compounds the following have been studied: bis(methacryl oxyethylenecarbonate)-ethylene glycol (OCEM); bis(methacryl oxyethylenecarbonate)1,4-butylene glycol (OCBM); bis(methacryl oxyethylenecarbonate)1,6-hexamethylene glycol (OCHM); and bis(methacryl oxyethylenecarbonate)-diethylene glycol (OCDM).

For comparison, a study was also made of the α, ω-dimethacryl-(bisethylene glycol) adipinate (MEA), which is an analog of the oligocarbonate methacrylate (OCBM) and whose molecule contains ester groups of noncarbonate type [1].

The synthesis of oligocarbonate methacrylates was performed by low-temperature condensation telomerization of an ethylene glycol monomethacrylate with bischloroformate glycols containing a variable number of methylene or oxyethylene groups. The reaction of a nonequilibrium condensation was carried out in a methylene chloride solution in the presence of pyridine, an acceptor for the hydrogen chloride evolved [13].

The structure of oligoesters was confirmed by results of elementary and physicochemical analysis, infrared spectroscopy, and gel-permeation chromatography. The elementary composition and some physicochemical constants of the synthesized compounds, which are colorless liquids or low-melting crystalline substances, are presented in Table 1. Some polymers with a conjugated system, i.e., polyphenylacetylene (PPA) obtained by catalytic polymerization of monomers on complex catalysts [14], and polyazophenylene (PAP) formed by the polydenitration of benzidine bisdiazonium [15], were used as structure-forming additives.

PCS was selected as a structure-forming additive because of the following considerations. The effect of small additions of PCS on the supramolecular structure, physicomechanical and adhesional properties, and also on the thermal stability of linear and crosslinked polymers is a matter of common knowledge [16, 17]. It has also

TABLE 1. Physicochemical Properties of Oligoesters

	Analysis						
Oligomer	C (%), exptl (calcd)	H (%) exptl (calcd)	Mean molecular weight, exptl (calcd)	Bromine number (Br g/100 g), exptl (calcd)	ρ (g/cm^3)	$n_D^{20°C}$	$\eta_{20°C}$ (cP)
OCEM	51.70	6.08	382	84.05	1.209	1.4650	272
	(51.33)	(5.93)	(374)	(85.39)			
OCBM	53.63	6.80	410	77.20	1.179	1.4645	230
	(53.73)	(6.51)	(402)	(79.44)			
OCHM	56.00	7.57	433	74.00	1.100	1.4585	[a]
	(55.80)	(7.00)	(430)	(74.40)			
OCDM	51.36	6.84	427	73.80	1.208	1.4654	309
	(51.66)	(6.26)	(419)	(76.36)			
MEA	58.00	6.90	397	80.70	1.135	1.4684	
	(57.70)	(6.90)	(370)	(86.60)			

[a] Crystalline, with mp 38°C.

been noted that PCS compounds contribute to a more ordered and closer packing of the polymeric chains and produce an effect on the system as a reinforcing filling material [18]. It should be stressed in this connection that, as has been shown [19], the addition of PCS does not produce any effect on hardening of the analogs of the oligomers (oligoester acrylates) under study.

When choosing possible structure-forming additives, it was also of interest to ascertain the effect on the formation and properties of coatings from oligocarbonate methacrylates of a ground sitall, an inorganic filling material with a rather highly developed surface (1 m^2/g).

Usually, the structure-forming additives were introduced into the oligomers in amounts of 1%. The effect of PCS in amounts of 2% on the coating microstructure was studied only for OCDM. The modifiers were thoroughly ground with a mortar and pestle in an oligomer medium until a system representing a nonseparating fine dispersion was formed. Film formation was carried out at a temperature of 80° C in the presence of a redox system represented by a cumene hydroperoxide and an accelerator (0.1% of a vanadium pentoxide solution in tributyl phosphate). Films of a definite thickness were obtained by applying, with the aid of a pipette, of a required quantity of the oligomer onto the surface made of Φ-1 glass. The inhibiting action of atmospheric air was suppressed by covering the surface of the film with cellophane.

The internal stresses were measured by the photoelasticity method with automatic recorder and estimated by the birefringence value of in substrate at the film boundary [20]. The coating structure was examined by electron microscopy by taking carbon-platinum replicas from the film surface subjected to oxygen etching for 20 min [7]. Adhesion of the coating was determined by the value of the limiting stresses causing a spontaneous separation of the film from the substrate [21]. The polymerization rate was followed by infrared spectroscopy, the deformational vibrations of the methacrylate α-CH_3 groups (1460 cm^{-1}) being used as an internal standard. The infrared spectra were taken during oligomer polymerization between two plates of sodium chloride by means of the UR-20 spectrophotometer. The coatings were aged under ultraviolet radiation by using P RK-2 lamps [22].

RESULTS

Figure 1 shows the kinetics of build-up of internal stresses during formation of the coatings with a different structure of the oligomeric block. The greatest internal stresses are observed for the coatings formed on the basis of the oligoester acrylate MEA. The coatings based on oligocarbon methacrylates show small differences in the values of the internal stresses.

The time required to attain maximum conversion for the oligomers containing methylene or ethylene oxide groups between the carbonate groups varies substantially. Thus, OCEM and OCBM undergo complete hardening in 40-60 min, while OCDM requires 150 min.

The kinetics of build-up of the internal stresses in the formation of the coatings from the oligomers under study was compared to that of consumption of the functional groups during polymerization as determined spectrophotometrically.

IR spectra show that the oligocarbonate methacrylate spectra, as distinct from α,ω-dimethacryl (bisethylene glycol) adipinate, include

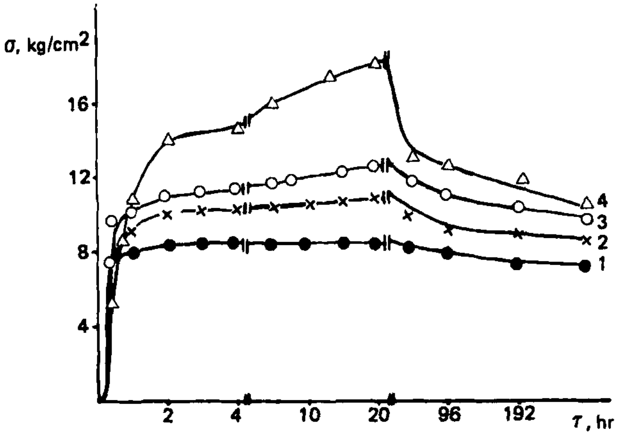


FIG. 1. Kinetics of build-up of internal stresses in the formation of the coatings from (1) OCEM, (2) OCBM, (3) OCDM, and (4) MEA.

band at 1760-1770 cm^{-1}, at the carboxylic group absorption band characteristic of carbonate groups. Despite the same number and arrangement of double bonds, ester, and methylene groups in the initial polymers, the intensity of the corresponding absorption bands depends markedly upon the size and flexibility of the oligoester chain portion located between the carbonate groups.

According to the intensity of the absorption bands in the region near 1650 cm^{-1} characteristic of the valence vibrations of C=C double bonds conjugated with a carbonyl group, and to the out-of-plane deformational vibrations of the hydrogen atom in the CH_2-groups, the oligomers under study can be arranged in the series OCEM > OCBM > OCDM.

With the structure of the oligomeric block being the same, the greatest number of bonds and their highest intensity in the spectra in the region of the vibration frequency typical of the ester bonds and methylene groups is observed for the coatings based on OCEM and OCBM, whose IR spectra do not differ significantly. It is probable that these lines point to the great intermolecular interaction realizable in such systems.

Evidently, for this reason, despite the same nature of the reactive groups in oligocarbonate methacrylates, the rate of formation of the corresponding coatings is markedly different. Coatings based on oligocarbonate methacrylates, although they involve a substantial

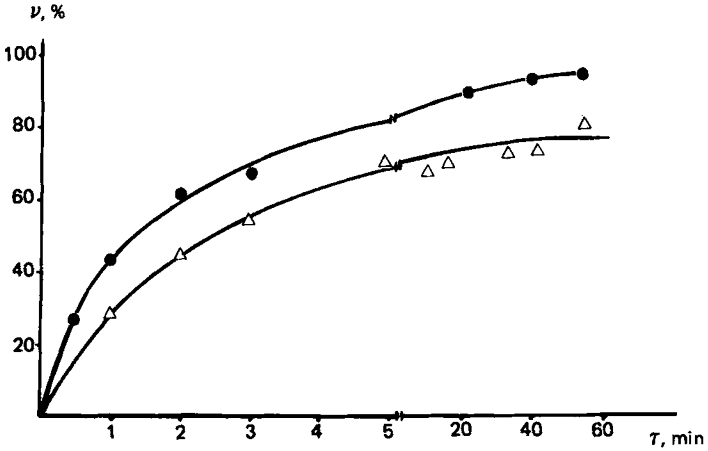


FIG. 2. Conversion of double bonds (ν) upon oligomer polymerization during hardening of coatings from (●) OCEM and (△) OCDM.

number of double bonds at the initial stages of polymerization, reveal fairly small internal stresses not exceeding 8-12 kg/cm^2 (Fig. 1). Under the same conditions, internal stresses in the coatings based on MEA increase more slowly, being about 16 kg/cm^2. This may be associated with the fact that oligocarbonate methacrylates, as compared to oligoester acrylates (MEA), constitute more crosslinked systems with a more active intermolecular interaction than the oligomers of the MEA type.

Figure 2 gives data on the consumption of the double bonds upon polymerization of oligomers during hardening. It is seen that the double bonds in the OCEM oligomers are consumed the most quickly. A lower rate and depth of hardening in the same period is observed for OCDM oligomer. Similar trends for the oligomers OCEM and OCDM can be established when evaluating a change in the absorption band intensity for the groups participating in the intermolecular interaction and manifesting themselves in the region 1180 cm^{-1} characteristic of ester groups.

The foregoing experimental data enable one to draw a conclusion that the reactivity of the oligomers under study in the process of coating formation and their conversion upon polymerization decrease as the length and flexibility of the oligomeric block increases, the converse of what is true for the three-dimensional bulk polymerization of acrylic oligomers [1].

TABLE 2. Effect of Oligomeric Block Structure on Physicomechanical Properties of Coatings

Oligomer	Length of oligomeric block (Å)	Adhesion (kg/cm^2)	Stress (kg/cm^2)
OCEM	19.41	70	8
OCBM	21.96	90	10
OCHM	24.51	30	10
OCDM	23.06	14	12
MEA	20.95	28	16

It is interesting to note that polymerization of the above oligoesters in a thin layer proceeds to fairly high conversions of the double bonds with no self-acceleration and that the gel effect appears only for the most slowly polymerizable oligomers (OCDM and MEA).

It is also of interest to establish the dependence of the adhesion of the resultant coatings on the chemical nature of the starting oligomer (Table 2). For oligocarbonate methacrylates, the dependence of the adhesion and stresses on the length of the oligomeric block is nonmonotonous and shows a maximum. The coatings based on MEA, which differs from OCBM by the presence of ester groups instead of carbonate groups, show a significantly weaker adhesion with approximately the same length of the oligomeric block. The most marked decrease in adhesion is observed for the coatings based on OCDM, characterized by the presence of an oxygen bridge in the oligomeric block.

These results demonstrate that in the formation of the adhesive interaction in the process of the oligomer-crosslinked polymer transition, the highest degree of adhesion is attained for the compounds forming the network from the more rigid structural elements.

At first glance, such a conclusion is inconsistent with the universally adopted ideas of the favorable role played by the macromolecular mobility in the realization of the adhesive interaction [18].

Figure 3 shows the microstructure of the coatings based on oligocarbonate methacrylates differing by the value of adhesion. The coatings based on OCEM and OCBM, with the shortest and the most rigid oligomeric blocks, are distinguished by an ordered pattern composed of anisodiametric structural elements. With an increase in the flexibility of the oligomeric block, for instance, as a result of

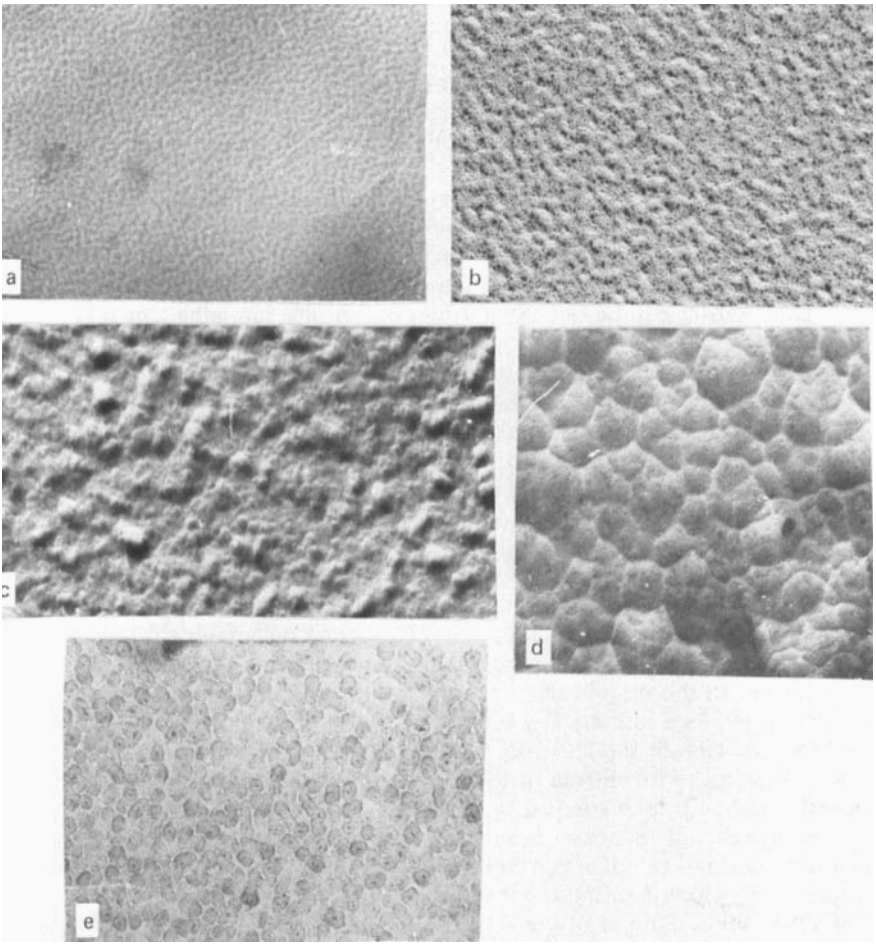


FIG. 3. Microstructure of the coatings from (a) OCEM, (b) OCBM, (c) OCHM, (d) OCDM, and (e) MEA.

introducing an oxygen bridge (as in OCDM) into the molecule or by extending the length of the block through added methylene groups (as in OCHM) there appear in the coatings, based on oligocarbonate methacrylates, a globular structure differing in the diameter of the globules and their packing density. Thus, for the OCHM-based coatings, the mean size of the globules is 150-300 Å (Fig. 3c). The OCDM-based coatings have a similar structure with a globule diameter of 500-1000 Å (Fig. 3d).

The globular type structure is also observed in the MEA-based coatings (Fig. 3e). These data agree with the results of the electron-microscopic examination of the polymeric block specimens based on oligoesters under study [23].

The results obtained upon studying the adhesion of the polymeric coatings based on the oligomers being discussed and their morphology make it possible to assume that the oligomers with rigid and short blocks form anisodiametric structures providing for the involvement of the greatest number of the active groups into the adhesive interaction.

The oligoesters with relatively flexible blocks are capable of forming supramolecular globular type structures whose surface seems to contain a fairly small number of active groups interacting with the substrate. It should be noted then, that the coatings from the oligomers with flexible oligoester blocks are distinguished in some instances by the size of the globular elements, their distribution, and the tightness of packing, factors which are responsible for the differences in their physicomechanical properties.

The development of coatings with an ordered structure from the oligomers with flexible oligomeric blocks and enhancement of their adhesive properties were performed by controlling the structure formation in the oligomeric arrangements through the addition of PCS. Figures 4 and 5 show the effect of the nature of the additives on the kinetics of the build-up and of relaxation of the internal stresses in the formation of the coatings from a oligomeric systems distinguished by the flexibility of its oligomeric block.

A significant increase in internal stresses during the formation of the coatings is observed in the coatings based on the OCEM oligomer, which has the most rigid and the shortest oligomeric block in the series of oligocarbonate methacrylates. In the coatings based on OCDM, which is characterized by a greater flexibility of the oligomeric block containing an oxygen bridge, the internal stresses during polymerization in the presence of additives are less pronounced, while in storage of the specimens at room temperature the internal stresses, due to the relaxation processes, become approximately equal to or substantially lower than those in the coatings from unmodified oligomer.

An increase in the length of the oligomeric block in a series of oligocarbonate groups by the ester groups change the nature of the effect of structure-forming additives on the kinetics of the internal stress growth during the formation of the coating. Thus, the

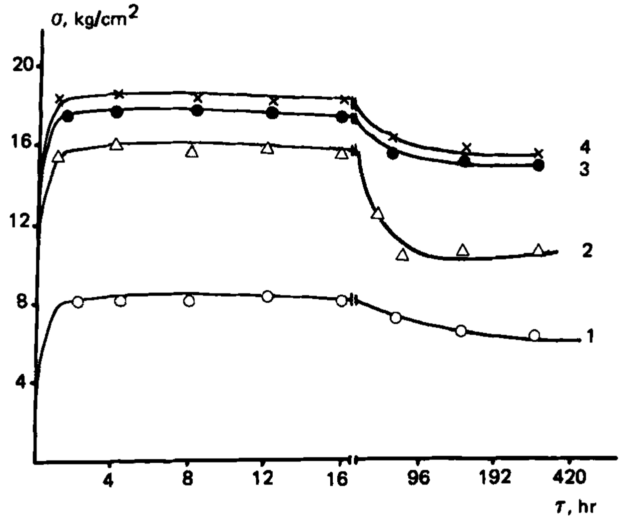


FIG. 4. Effect of the nature of the additives on the kinetics of build-up and relaxation of the internal stresses during the formation of coatings from OCEM; (1) no additives; (2) with 1% polyazophenylene; (3) with 1% polyphenylacetylene; (4) with 1% sitall.

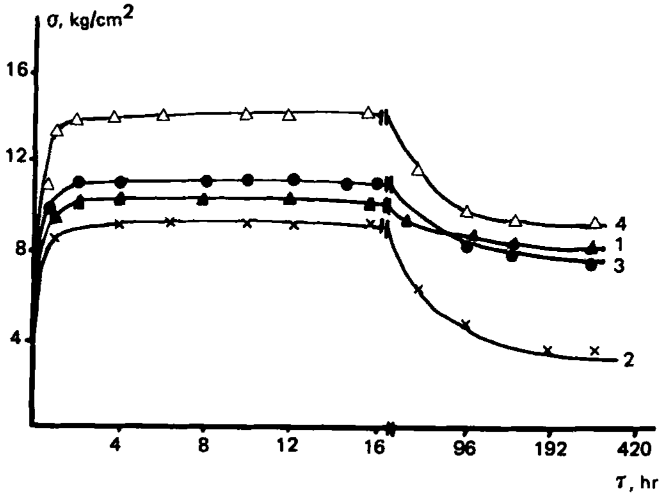


FIG. 5. Effect of the nature of additives on the kinetics of build-up and relaxation of internal stresses during formation of coatings from OCDM: (1) no additives; (2) with 1% sitall; (3) with 1% polyazophenylacetylene; (4) with 1% polyphenylacetylene.

TABLE 3. Variation in the Coating Adhesion Depending on the Nature of Structure-Forming Additives

Oligoester coating	Coating adhesion with various additives (kg/cm^2)			
	None	Polyphenyl acetylene	Polyazo-phenylene	Sitall
OCEM	70	28	27	37
OCDM	14	30	24	20
OCBM	90	36	50	56
MEA	28	20	20	18

introduction of additives into the OCBM oligomer tends to decrease the internal stresses both at the formation stage at a temperature of 80°C and upon storage of the specimens at room temperature. A decrease in the internal stresses in the presence of the additives is especially noticeable for the MEA-based coatings.

The polymerization of the MEA-based coating is peculiar, in that the modifiers not only reduce the internal stresses but considerably accelerate film formation.

The flexibility and the length of the oligomeric block have a significant effect on the type of dependence of adhesion on the nature of the modifiers. It is seen from Table 3 that introducing the additives into the oligomers of a series of oligocarbonate methacrylates with a rigid oligomeric block decreases adhesion. This effect is especially pronounced with the coatings based on OCEM, which has the shortest and the most rigid block. With an increase in the length of the oligomeric block, e.g., for the OCBM- and MEA-based coatings, a decrease in the value of adhesion is less perceptible.

A variation in adhesion is of another nature for the coatings based on OCDM whose oligomeric block is distinguished, among all the oligomers under study, by the greatest flexibility. As can be seen from Table 3, additives introduced into this system greatly increase adhesion.

It is equally interesting to note that some modifiers produce a marked effect on the process of polymerization of oligocarbonate methacrylates in a thin layer. As follows from Fig. 6, the presence of polyphenylacetylene increases the polymerization rate and conversion of the OCDM oligomer. These data are in accord with the results a study of the effect of the polymeric compounds with a conjugated

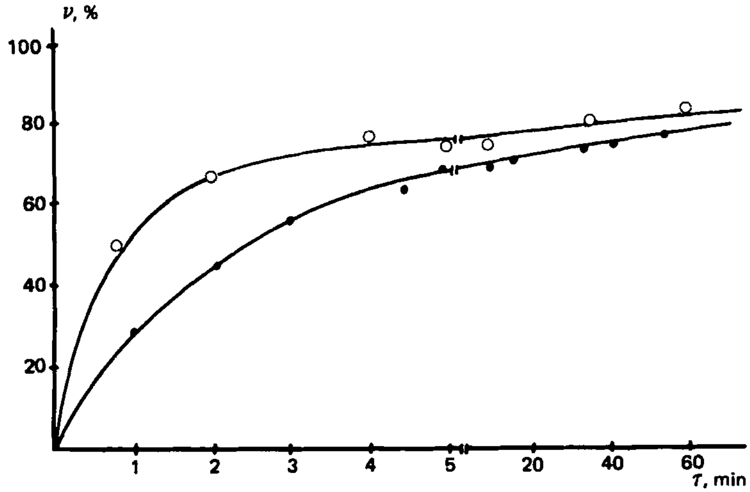


FIG. 6. Conversion of double bonds (ν) on polymerization of (○) an unmodified OCDM (●) OCDM with the polyphenylacetylene as additive.

system on the kinetics of the oligoester acrylate bulk polymerization [1].

Microstructural studies were conducted to establish specific features of the effect of various modifiers on the mechanical properties of the coatings based on oligoesters characterized by the flexibility of the oligomeric block.

As shown in Fig. 7, the introduction of an additive into OCEM hinders the formation of a crosslinked structure from anisodiametric structural elements which was observed in the absence of the modifiers and promotes their aggregation to large supramolecular formations of a globular type.

A different effect of the additives is observed when investigating the structure formation of the coatings based on OCDM oligomers. In this case, the introduction of modifiers leads to formation of a more ordered structure from anisodiametric type elements, compared with the nonuniform globular structure formed without modifiers with a globule diameter of 500-1000 Å (Fig. 8). Taking OCDM-based coatings as an example, it has also been found that an increase in the concentration of the PCS in the coating, up to 2%, gives rise to anisodiametric elements of a far greater size (Fig. 8).

It could be expected that the various effects of the modifiers of

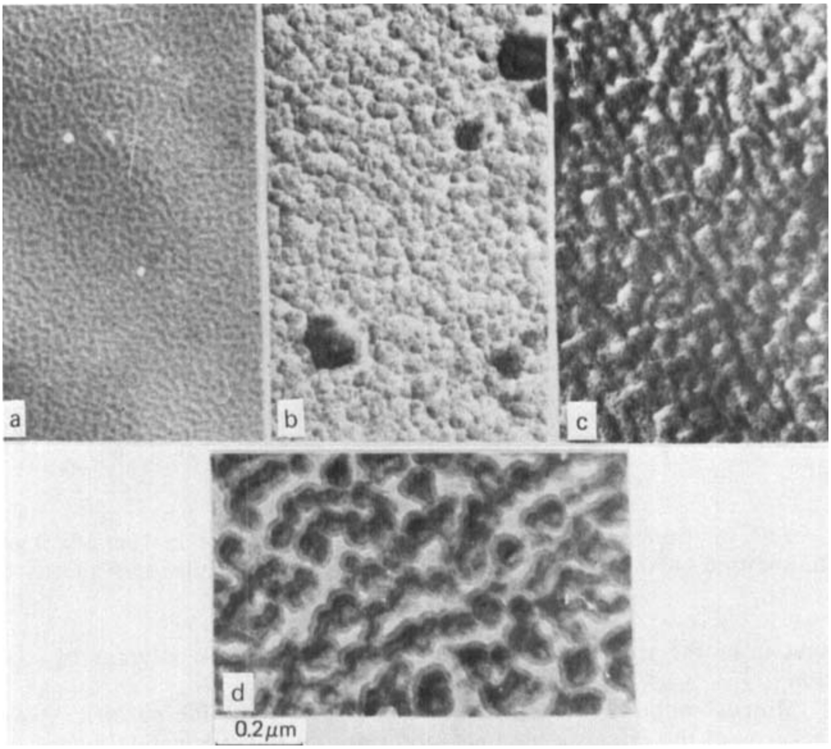


FIG. 7. Microstructure of coatings from (a) OCEM alone and with additives; (b) 1% polyazophenylene; (c) polyphenylacetylene; (d) sitall.

structure formation in the oligomeric systems distinguished by flexibility of the oligomeric block are bound to have a marked influence on other properties of the coatings, particularly on time of aging under ultraviolet irradiation.

Figure 9 lists data on the variation in the internal stresses of the oligomers under study as a result of ultraviolet irradiation. It is seen that in the absence of the modifiers a sharp decrease in the internal stresses in the process of the coating aging, probably associated with the polymer destruction [22], is at first observed for the OCDM-based coatings (Fig. 9). Durability of these coatings under experimental conditions is less than 170 hr.

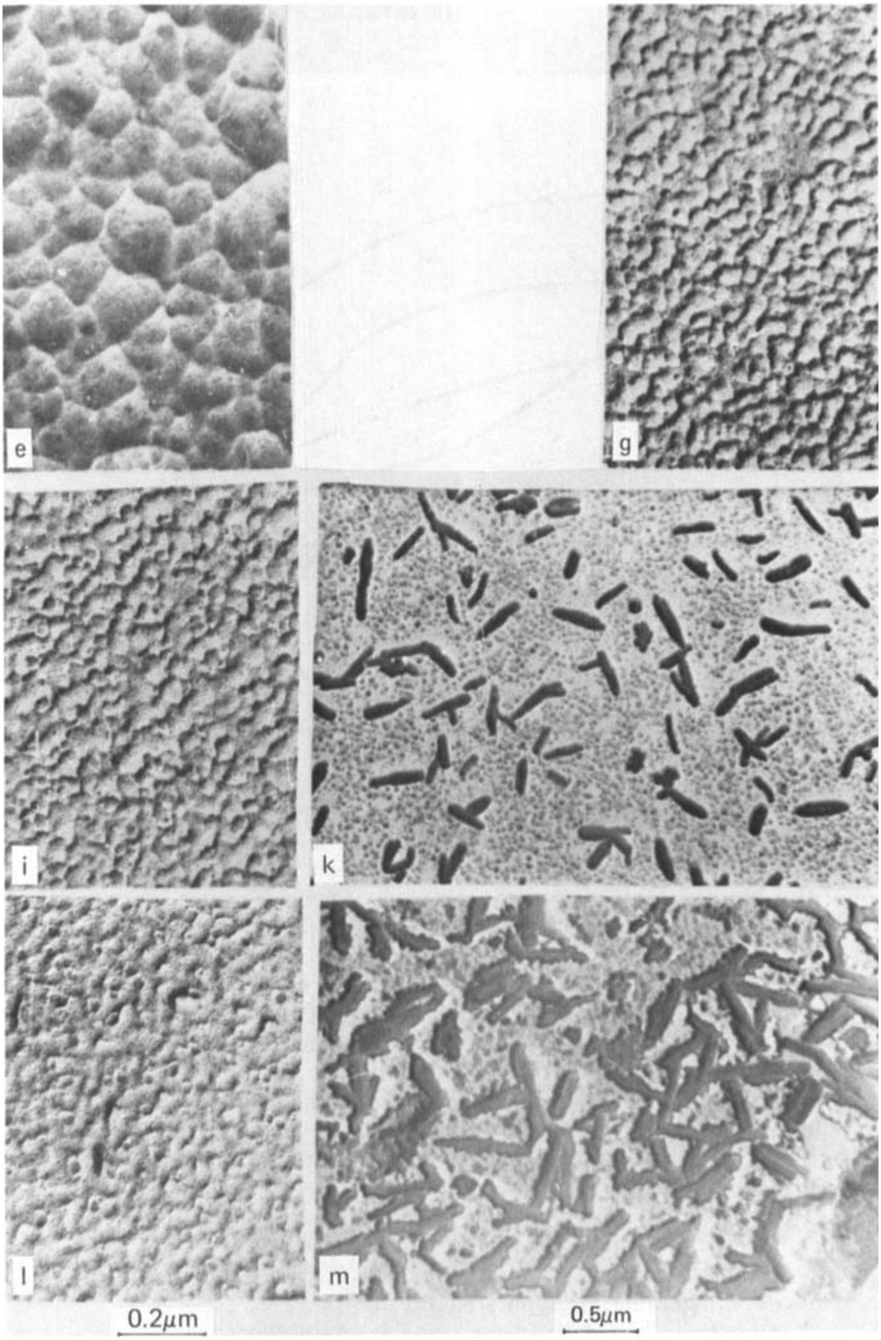


FIG. 8. Microstructure of the coatings from (c) OCDM alone and with additives; (i) 1% polyazophenyl; (l) 1% polyphenylacetylene (g) 1% sitall; (k) 2% polyazophenylene; (m) 2% polyphenylacetylene.

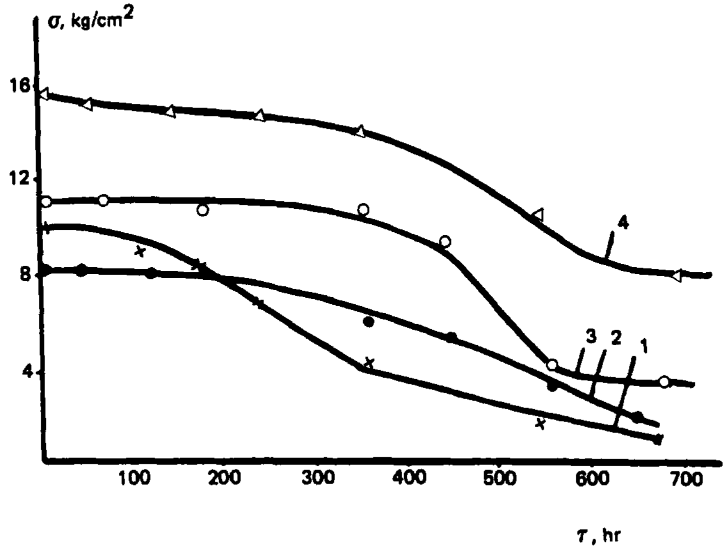


FIG. 9. Variation in the internal stresses during aging of the coatings from (1) OCDM, (2) OCEM, (3) OCBM, and (4) MEA.

Resistance to aging becomes higher in coatings based on oligomers with more rigid oligomeric blocks and a more ordered microstructure (Fig. 9). These coatings withstand about 450 hr irradiation without any noticeable change in their physicomechanical properties.

The manner in which the additives affect the durability of the coatings based on the oligomers under study varies considerably. Figures 10 and 11 give data on the variation in the internal stresses in aging of the OCEM- and OCDM-based coatings in the presence of various modifiers. One can see that the introduction of the additives into OCEM greatly affects the durability of the coatings as compared to that of coatings based on a nonmodified oligomer. The pattern observed is probably associated with a lower adhesion of the coatings based on a nonmodified oligomer and their spontaneous separation during aging.

By contrast, the introduction of additives into OCDM enhances the durability of the corresponding coatings, especially in the presence of polyphenylacetylene, which favors network formation from the ordered anisodiametric type structures.

For coatings based on OCBM- and MEA-oligoesters, which occupy

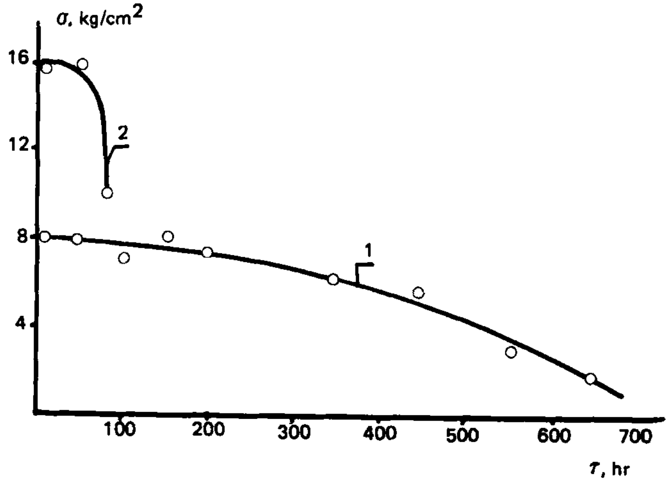


FIG. 10. Effect of structure-forming additives on the internal stresses during aging of coatings from OCEM: (1) starting specimen; (2) with 1% polyazophenylene.

a position intermediate between OCEM and OCDM with respect to flexibility of their oligomeric block, the introduction of additives enhances durability due to a relatively small decrease in adhesion with a simultaneous drop in the internal stresses in the system. The effect of increasing durability in the presence of the modifiers for these systems is less pronounced, however, than for the systems based on OCDM.

These results show conclusively that the mode of action of the additives on the structure and properties of the coatings is significantly dependent on the nature and flexibility of the oligomeric block. The introduction of additives into the oligoesters with short and rigid oligomeric blocks hinders formation of the crosslinked polymer from the ordered structures of an anisodiametric type and favors the formation of a globular structure with a low adhesion and high internal stresses.

The introduction of additives into oligomers with more flexible fragments of the oligomeric block causes an orientation effect of the oligomer molecules. This leads to the formation of a network of anisodiametric-type structures, followed by a slight increase in coating adhesion, with a small increase in the internal stresses

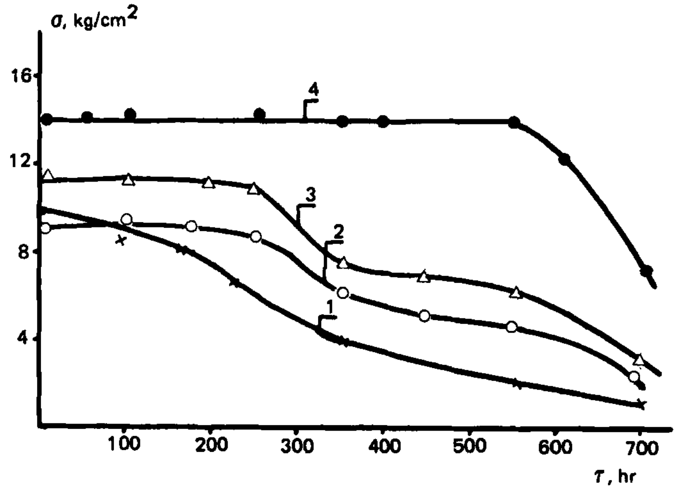


FIG. 11. Effect of structure-forming additives on the internal stresses during aging of coatings from OCDM: (1) starting specimen; (2) with 1% polyazophenylene; (3) with 1% polyphenylacetylene; (4) with 1% sitall.

during coating formation and significant relaxation of these stresses during storage of the specimens.

DISCUSSION

The effect of the supramolecular organization of liquid oligomers on their physicomechanical properties and on the structure and properties of the resultant crosslinked polymers has been shown earlier [24].

The results were supported and further developed in a number of investigations showing clearly the effect of the associated formations on the adsorption of a series of oligomers and the properties of boundary layers of the corresponding crosslinked polymers [25].

On taking the above considerations into account, we may relate the laws of polymerization observed by us in a thin layer in contact with a glass substrate to the differences in the structure of the adsorption layers of the associated oligocarbonate methacrylates with the longer chains as compared to their lower molecular weight homologs.

According to Lipatov and Sergeyeva [25], the associated oligomers interact with the surface with a smaller number of groups and retain a greater mobility, so they are consequently, less ordered than the individual molecules adsorbed by the surface.

In the case of a kinetically favorable molecular orientation in the adsorption layer, the surface acts beneficially on the rate of polymerization as compared to the bulk polymerization.

Along these lines, it is possible to gain an insight into the reason for the absence of self-acceleration which is observed during three-dimensional polymerization [1] in the process of oligomer hardening on a glass substrate.

According to earlier investigations [26-28], the formation of crosslinked polymers proceeds through the stage at which there appear soluble branched polymers (so called "β-polymers") determining their structure and properties. Such a concept allows one to conclude that an increase in flexibility of the part of the oligomeric block located between the polymerizable groups and a weakening of the intermolecular interactions will cause a more coiled conformation of the β-polymer and a globular structure of the resultant crosslinked polymers. An increase in the rigidity of the β-polymer, due, for example, to the rigidity of the oligomeric block fragments and their high intermolecular interaction, results in the formation of the more ordered and more closely connected anisodiametric structural elements. It is obvious that in the former case contact of functional groups with the surface occurs with more difficulty and, consequently, the adhesion and stresses in the boundary layer decrease.

The foregoing considerations may account for a somewhat unexpected result of the present study: the closer and more rigid crosslinked polymers exhibit the more anisodiametric supramolecular formation and the higher values of adhesion.

Thus, we have studied the effect of the substrate on the polymerization kinetics of the oligoester acrylates with a regular alternation of the active groups and also on the structure and properties of crosslinked polymers formed under conditions of adhesional interaction.

The reactivity of the oligoester acrylates under study and their conversion increase in the formation of the coatings from the short and rigid blocks which are better adsorbed on the substrate and form a network from the ordered anisodiametric structural elements with high adhesive properties as distinct from the globular structures arising upon the formation of the network from the oligomers with flexible blocks.

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