Morphology of Oligomers and Their Network Polymers

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SUMMARY

The morphology of di(4-methacryloxyethylene carbamate
toluylen-2-carbamic) esters of oligoethylene glycols
(OUM) with different molecular weight, of their net-
work polymers and of model oligomers without metha-
crylic groups was studied. The supermolecular struc-
ture of oligomers is found to depend on molecular
weight. Globular structure is typical for low molecu-
lar weight oligomers with $\overline{M}_n \gneqq 1200$. The structure of
crystalline samples with $\overline{M}_n = 1600-3600$ is lamellar.
The latter is retained on melting. It is transformed
into globular structure at a temperature much higher
than the melting point. A correlation exists between
the morphology of polymerizable oligomers and their
network polymers.

The process of network formation from oligomers is
extremely complicated. Irrespective of the mechanism
it is influenced by MWD, FTD, intermolecular interacti-
on and a number of other factors. The interconnection
between the morphology of polymerizable oligomers and
the supermolecular structure of their crosslinked
polymers has not been sufficiently studied. Informati-
on about this connection facilitates phenomenological
understanding of the network formation process.

EXPERIMENTAL

The OUM's and model compounds (OUE) were prepared by
reaction of different molecular weight oligoethylene
glycols with 2-isocyanate toluylene-4-methacryloxy-
ethylene (or 4-ethyl) urethane (Tabl.1) (ZEMSKOVA et
al. 1973); network polymers were obtained by radical
polymerization of OUM's (MATVEEVA et al. 1974). The
supermolecular structure of liquid oligomers and melts
was fixed by fast freezing of samples with liquid nit-
rogen; micrographs of replicas of oligomer and polymer
samples were obtained with an EUMB-100B electron mic-
roscope; the fracturing of glassy oligomers and depo-
sition of the carbon film on the fracture surface were
carried out under vacuum at -150 - -160°C (MATVEEVA,

KISELEV et al. 1978); platinum-carbon replicas of po-
lymer samples were prepared by procedure (KISELEV et
al. 1966); a small-angle X-ray scattering study was
carried out with KRM-1 using CuK_α -emission; the ex-
perimental data were corrected by a known method
(GUINIER,FOURNET 1955).

TABLE 1

Characteristics of OUM's, model oligomers
and mixtures of latters

Formulas and marks	$\bar{n}$	$\bar{M}_n$ *	T_m, °C	Crystalli-nity degree at 20°C,%
$\left[CH_2=CCH_3COOCH_2CH_2OCONH\langle\bigcirc\rangle CH_3 \atop NHCO(OCH_2CH_2)_{n/2}\right]_2$				
OUM	13	1200	6	liquid
	37	2250	41	30
	68	3600	56	50
$\left[CH_3CH_2OCONH\langle\bigcirc\rangle CH_3 \atop NHCO(OCH_2CH_2)_{n/2}\right]_2$				
OUE	3	590		liquid
	13	1040		liquid
	68	3400	43-45	50
Mixtures of OUE's M_n = 590 and 3400				
weight ratio 1:20			39-41	40
1:1			30-32	liquid
$\bar{M}_n$ = 1040 and 3400				
weight ratio 1:20			41-42	55
1:1			39-40	35

* M_w/M_n = 1.07-1.2.

RESULTS AND DISCUSSION

The oligomers depending on molecular weight are vis-
cous liquids or waxy compounds. The supermolecular
structure of glassy low molecular weight OUM ($\bar{M}_n \approx 1200$)
is characterized by the presence of globular formati-
ons ranging from 100 to 500Å.For instance, the size of
globules for OUM with $\bar{M}_n$ = 1200 is 180-200Å (Fig.1).
The morphology of crystalline OUM with M_n=1600-3600 is
lamellar.The thickness of lamellae of the oligomer
with $\bar{M}_n$=1600 is 100-130Å;of OUM with M_n=2250, 150-
-180Å and of OUM with M_n=3600,to 80-100 Å (Fig.1).The
lamellar structure of OUM is retained on melting and
on subsequent cooling down to the room temperature.In
some cases the melts do not crystallize and remain in
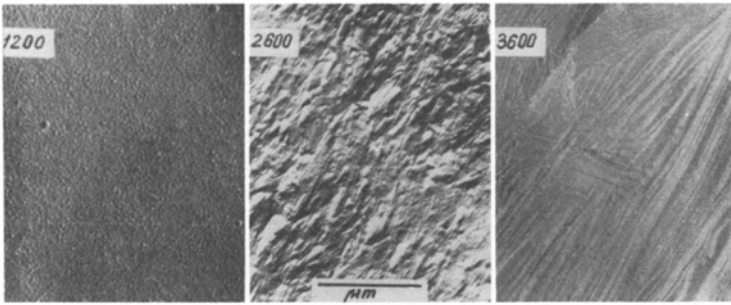the liquid-crystalline state (Fig.2).The dependence of

Fig.1.Morphology of different molecular weight
oligomers

oligomer morphology on the temperature was studied in
order to estimate the stability of a supermolecular
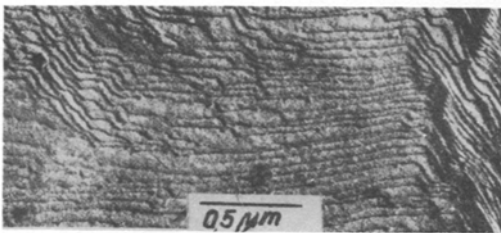organization of oligomers and to find the correlation
between the morphology of oligomers and their network polymers.Model oligomers without methacrylic groups were synthetized to exclude the polymerization of OUM's. Micrographs of fracture replicas of vitrified oligomer melts heated to ~10° and ~100° above the melting points are demonstrated in Fig.3. The thickness of lamelae of vitrified melts is close to the values typical

Fig.2.Morphology of oligomers
with M_n = 2250 in a liquid-
crystalline state.

for the same oligomers in the crystalline state.With
further increase of the temperature,globules emerge
on the surface of the lamellae.The lamellar structure
is completely transformed to a globular one at a tem-
perature much higher than the melting point (MATVEEVA,
KISELEV et al. 1979).
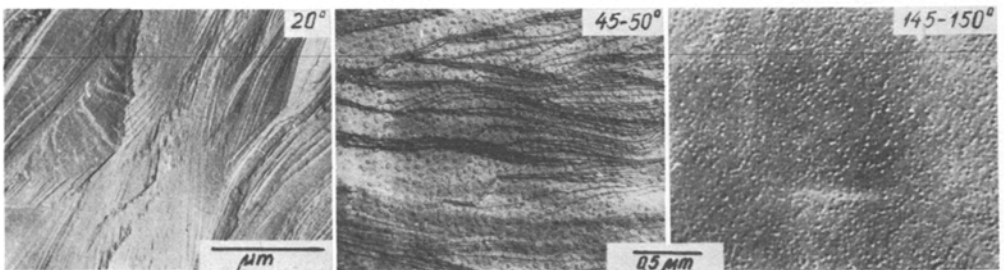
Fig.3.Temperature transformation of the morphology of
the oligomer with $\overline{M}_n$ = 3400.
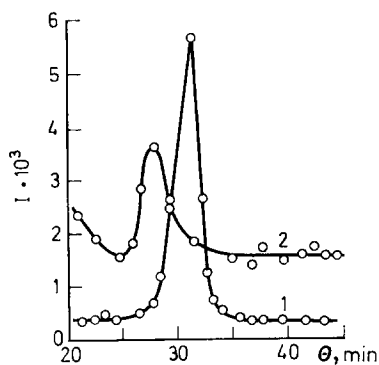
Fig.4.Small-angle X-ray scattering curves for oligomers with $\overline{M}_n$=1200 (2) and $\overline{M}_n$ = 2250 (1).

Small-angle X-ray scattering curves display a distinct maximum which indicates the presence of oligomer organization at the supermolecular level. The position of the maximum varies with the molecular weight of the oligomer (Fig.4).The value of the large period for the oligomer with $\overline{M}_n$ = = 1200 is 150Å and for the oligomer with $\overline{M}_n$ = = 2250,170Å.The results of the small-angle X-ray scattering study of oligomer morphology confirm the electron microscopy data.

The supermolecular organization of the mixtures of oligomers is controlled by the molecular weight and the ratio of initial components. The presence of lamellar structure (thickness ~100Å) decorated by globules of the low molecular oligomer (d≤100Å) is characteristic of the mixture of the OUE's with $\overline{M}_n$=600 and 3400 enriched by the high molecular component (weight ratio 1:20) (Fig.5a).The morphological pattern essentially varies when a part of the low molecular weight oligomer increases. Separate lamellar incorporations typical of the high molecular ingradient are observed for the mixture of components taken in equal parts by weight. At the same time the background of the sample consists of globules (homogeneous in size) of the low molecular weight oligomer (Fig.5b).
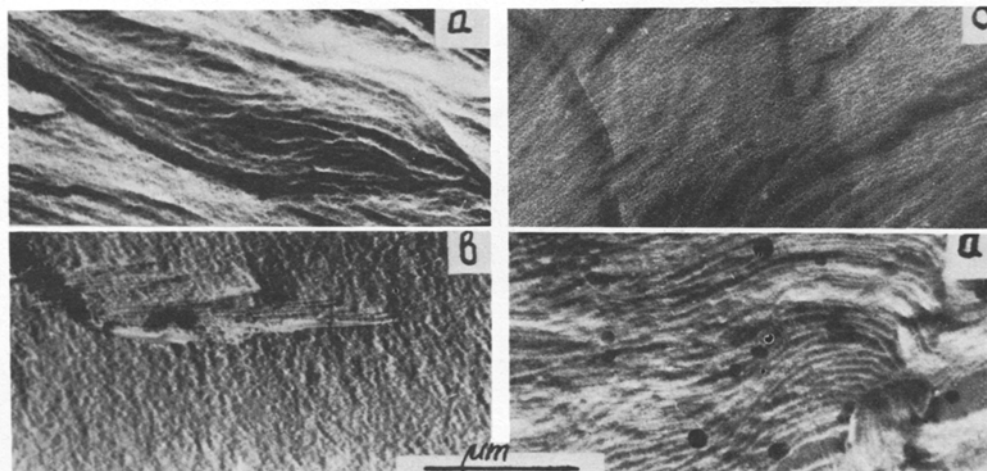

Fig.5.The morphology of mixtures of oligomers as a function of molecular weights and composition.

The increase in molecular length of the low molecular part of the mixture ($\overline{M}_n$=1040 and 3400) practically do not influence the morphology of the high molecular weight component at a small content of the former (weight ratio 1:20). In this case the distinctly form-ed lamellar structure is retained; the thickness of lamellae is close to the value for the crystalline state of this component; however, accumulation of the globules and erosion of the lamella edges in indivi-dual separate regions are observed (Fig.5c). The vari-ation in the oligomer ratio in the mixture towards the low molecular weight component (weight ratio 1:1) leads to essential looseness of the structure - the thick-ness of the lamellae increases and the sharpness of the lamella edges disappears (Fig.5d).

Thus, the morphology of the oligomers is controlled by their molecular weight. The studied oligomers are cha-racterized by the chain regularity, by the terminal groups capable to form H-bonds and by the narrow MWD. All that ensure preservation of the order in the oli-gomer melts at temperatures higher than the melting points. Fractionation in size of the macromolecules is observed for mixtures of different molecular weight oligomers prepared by mixing of the solution of the components and by subsequent evaporation of the sol-vent. As a result the morphological pattern represents a combination of the supermolecular elements charac-teristic of the initial oligomers.

There exists a connection between the supermolecular structure of crosslinked polymers and the morphology of initial oligomers. Network polymers prepared by curing low molecular weight oligomers are composed of globules and the different formations consisting of coalesced globules. The morphological pattern of po-lymers obtained from oligomers having a lamellar struc-ture does not differ from the structure of the initial oligomers. The lamellar structure is observed also for an amorphous polymer with the value of interstitual chains $\overline{M}_c$ = 1600 (Fig.6).

The supermolecular structure network polymer obtained by curing the mixture of oligomers with different mo-lecular weight is characterized by the presence of va-rious structural elements. Regions of globular and "spherulite"-like formations have been found in an amorphous polymer based on the mixture of oligomers with M_n=670 and M_n=6600 taken in equal parts by weight (Fig.7a,b). A polymer obtained by curing the mixture of equal parts by weight of OUM's with M_n = 750,1600 and 3600 is amorphous and has a globular - lamellar structure with eroded boundaries after two-week stand-ing at room temperature. After more than a three-year standing this polymer crystallizes to a small degree of crystallinity ($<$10%) and its structure remains
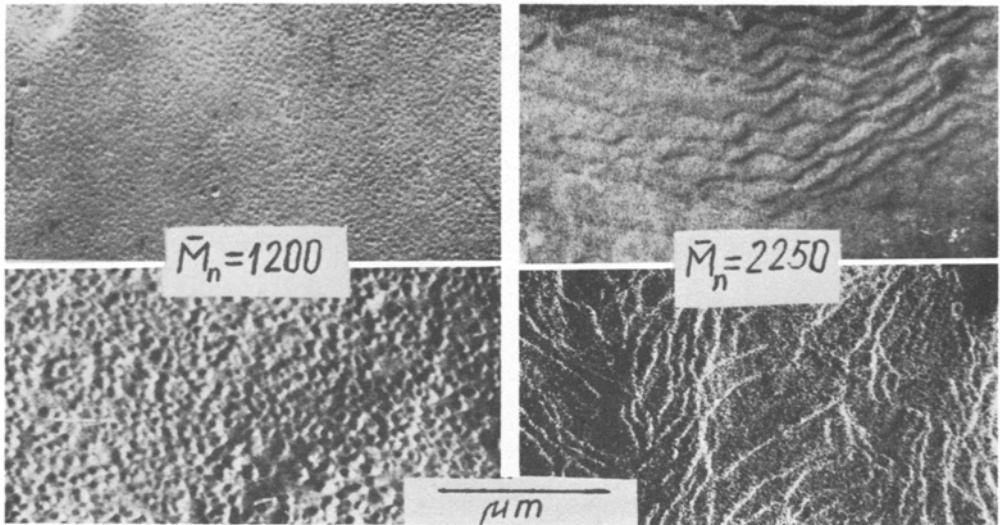
Fig.6.Correlation between morphology of oligomers and their network polymers.

globular, but the lamellae become more dictinct (Fig. 7c). A similar phenomenon is observed for the polymer prepared from a mixture consisting of eight oligomers with narrow MWD and different molecular weight ranging from $M_n = 670$ to $\overline{M}_n = 6600$. After two-week standing this polymer is amorphous and has a globular structure. After long standing it partly crystallizes ($< 10\%$); rather well formed lamellae are present in its structure together with globular formations.
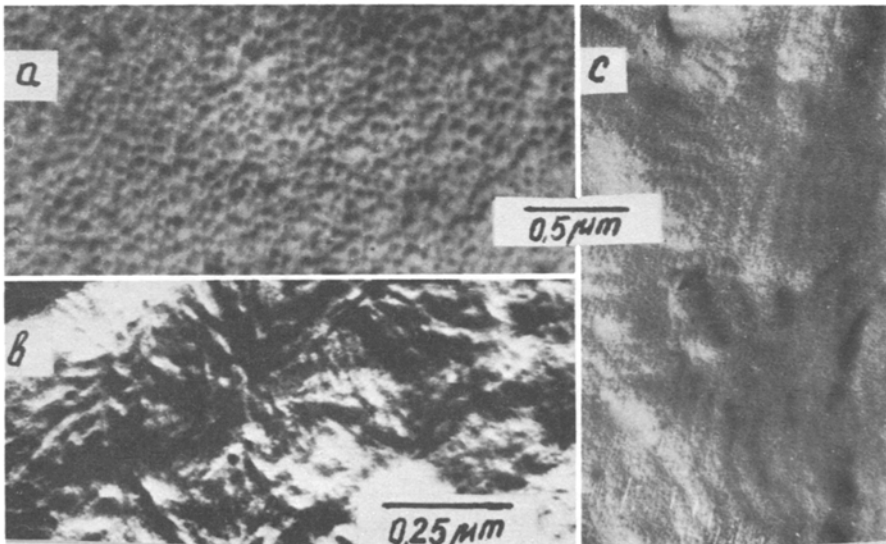

Fig.7.Morphology of network polymers based on mixtures of oligomers.

The following phenomenological pattern of the formation
of crosslinked polymers by polymerization of α, ω -
bis unsaturated oligomers may be suggested (BERLIN
1977; MATVEEVA 1977):

During crosslinking polymerization of low molecular
weight oligomers the resulting primary polymethacry-
lic chains, having an oligomeric pendant in every unit,
coil and aggregate with each other. The growth of mac-
rochains continues due to consumption of the oligomer
immobilized in the coils and of the methacrylic groups
in the pendant oligomer blocks. The macrochains branch
out, form cycles, and crosslink together. As a result,
stabilization of these aggregates takes place. In the
course of this process the density of aggregate par-
ticles gradually increases as a result of their con-
traction. Simultaneously the syneresis of the soluble
polymerizate may take place.The individual particles
become linked together by polymethacrylic tie-chains
and oligomeric blocks. When the number of such par-
ticles and of the branched and tie-chains becomes suf-
ficient for immobilizing the liquid reactant, there
occurs gelation, and the system loses its fluidity.
As a result, a microheterogeneous three-dimensional
crosslinked system is formed and highly crosslinked
microparticles are interconnected by zones having an
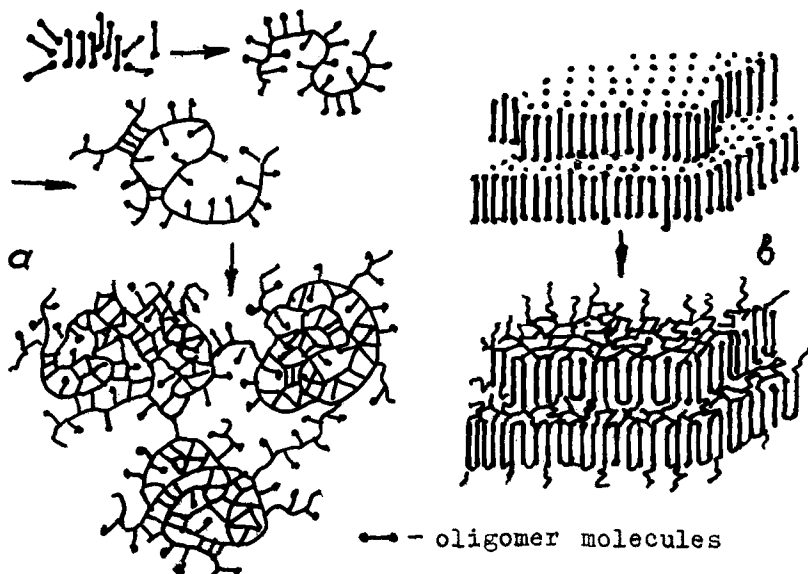essentially lower crosslinking density.

$\longleftrightarrow$ - oligomer molecules

Fig.8. Scheme of the network formation from oligo-
mers.

In the case of crystalline oligomers their transition on melting to the liquid-crystalline state with lamellar structure is observed. In such systems the polymerization process develops in the interlayer zones where terminal functional groups are concentrated. The mobility of the terminal groups of oligomeric molecules in these zones is quite sufficient for realization of the process of propagation and conformational transformations of growing primary macrochains. As a result of three-dimensional polymerization, the terminal groups of oligomeric molecules become cross-linked and lamellar structure of the liquid is fixed in the polymer.

The process of the network formation in the case of oligomeric mixtures includes elements of the mechanisms described above. The supermolecular structure of such polymers is either completely globular, or it consists of combinations of globular formations with lamellae not well defined or of other structural elements. However, in spite of considerable disorder and the limited mobility of interstitual chains, a gradual increase of order in the system, a crystallization of long-chain oligomeric blocks, and a formation of lamellar structure regions may be observed in the network polymer.

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