ACHIEVEMENTS AND PROBLEMS IN THE FIELD OF HIGH
POLYMER MODIFICATION BY POLYMERIZABLE OLIGOMERS

Alfred A. Berlin, Semion M. Mezhikovskii

Institute of Chemical Physics, Academy of Science USSR,
UUSR, 117334, Moscow, Vorobyevskoe Shaussee, 2b

Abstract – The exploratory problems of modification of high
polymers with polymerizable oligoesteracrylates (OEA) and
modern state of the art are reviewed. Various aspects of
compatibility, phase equilibrium and rheology properties of
polymer – oligomer compounds are considered. Probable mecha-
nisms of OEA transformations taking place in polymer matrix
during polymerization, as well as structure and properties
of microheterogeneous composites formed are discussed. A
number of examples illustrating the effect of mix components
on the mechanical and processing properties of polymer –
oligomer systems are given. Major possible ways of explora-
tion of heterogeneous three-dimensional polymerization (co-
polymerization) in nonequilibrium viscous media are compared.

The present-day stage of development of the "science of polymers"
(1), in its applied aspect particularly, "polymer study of materials", is
characterized rather by a search for rational ways of polymer material pro-
duction providing the maximum realization of the properties of already tes-
ted in practice large-tonnage polymers, than by working out new methods of
synthesis of new polymers, as was the case, for instance, in 30-50-ies.

For these purpose physical and chemical modification of polymers holds the
greatest promise.

Among different aspects of polymer modifications, which have been recently
developed, the so-called principle of "time plasticization" (2) is of great
practical and scientific interest. This not very felicitous but adopted
term in scientific and engineering literature serves for indicating the ap-
proach based on applying polymerizable oligomers (PO) as modifiers. It al-
lows one to solve simultaneously several important problems: to intensify
the treatment of polymers and to regulate the properties of end products.

The principal essence of this method is that a liquid and low-melting poly-
merizable oligomer introduced into a linear polymer serves first as a plas-
ticizer, facilitating thus the treatment of the polymer-oligomer mixture,
and then at the stage of molding the sample is consolidated (hence, the term
"time") and changes to a cross-linked polymer which is related with the ini-
tial polymer substrate by chemical and (or) physical forces. It is this fact
that defines the new properties of modified polymers. It should be noted
that, since the reactivity of functional groups and their number, and also
the dimension and nature of the oligomer block can be predetermined a priori,
there arises a possibility of regulating the properties of intermediate and
end products of the system.

Thus method of linear polymer modification has readily gained wide applica-
tion in practice for production of glues (3, 4), rubbers (5-10), adhesive
for reinforced plastics (11-13), dielectric compounds (14, 15), films and
covers (16), construction plastics (17, 18) and of other polymer materials
(19, 24) possessing the complex of new properties. However, for some time
the choice of components has been based on an empirical approach. Systema-
tic investigations of structures and properties of the initial polymer-oli-
gomer mixture and of regularities of the component conversion in the pro-
cess of hardening have started later (25-33). The experience gained so far
makes it possible to generalize the main stages of work which should be
done in this field and formulate several general problems, their statement
being necessary for elucidating the interrelation between the structure of
polymer-oligomer systems and their properties. Some of these approaches are

presented in the diagram (Fig. 1). It seems that they are of a gene-
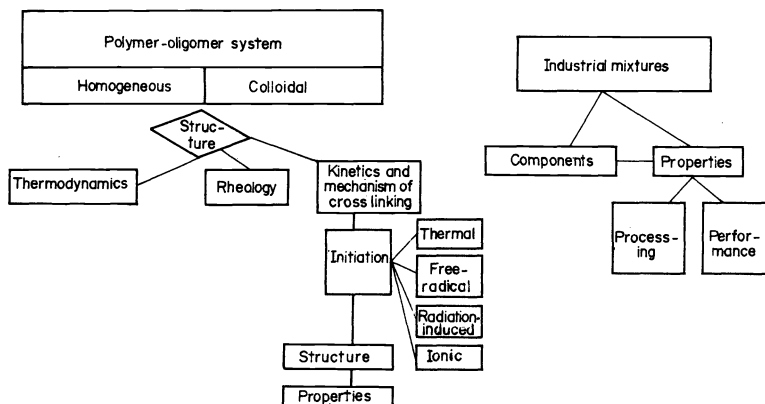ral sense for investigating the polymer modification.

Fig. 1. Diagram of polymer-oligomer systems exploration

On mixing (see Note a) a polymer with an oligomer homogeneous or colloid
systems may be formed. They may be nonequilibrium or pseudoequilibrium (tak-
ing account of the high times of relawation). Therefore, it is required that
thermodynamic characteristics of the system should be known, and first of
all diagrams of phase state, rates of diffusion, heats of mixing, solution,
equilibrium constants and so on.

The structure of polymer-oligomer mixtures, as a result of thermo-dynamic
functions of the system and its colloidal-chemical state, defines both
rheology and kinetics of further hardening.

In a most general case the hardening is reduced to concurrent processes of
three-dimensional homo- and inoculation PO polymerization in a very viscous
polymeric medium.

A radical difference of the PO transformations in the polymer matrix from
their block-homopolymerization investigated in detail (25) is that the pro-
cess from the beginning proceeds in a highly-viscous medium under condi-
tions of nonequilibrium microheterogeneous separation. Polymerization fixa-
tes nonhomogeneity. The structure and propecrties of the hardened material
depend thus on the characteristics specifying the degree of withdrawal of
the system from the state of equilibrium.

With polymerization of semifunctional oligomers in polymeric media there
arise the same problems of kinetics and topology of lattice formation, as
those with the PO block-polymerization, but complicated by the presence of
another phase.

A most important problem is the study of the processes occurring in real
multi-component polymer-oligomer systems. It consists in the effect of fil-
ters, in case they are necessary, plasticizers, inhibitors, antioxidants,
antiscorchings and so on.

These are some primary scientific problems, their systematic study and solu-
tion being indispensable for the development of physical-chemical founda-
tions of the oligomer-polymer principle of high polymer modification.

Though information is available in literature on application of different
classes of PO (see Note b), epoxy, allyl, vunyl, diene, urethane containing,
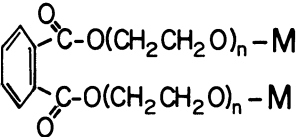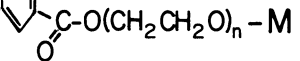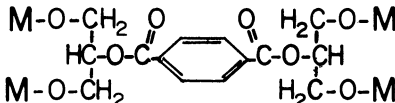
Note a. The method of mixing the components affects the properties and re-
         quires a particular cinsideration.
Note b. The results of   elastomer modification by polycondensation oligo-
         mers are summarized in the monograph (34). The problems of elasti-
         fication of stiff-chain polymers with oligomer bearing elastic
         blocks are considered in the review (35).

organosilicon and other PO, for modification of high polymer properties (see, for instance (37–41), this paper deals mainly with modification of high polymers by oligoesteracrylates (OEA). There are two reasons for such a choice:

1) From a number of considerations OEA, including chemical, economical, toxicological and other reasons (for detail see (36), are most promising; 2) in this field the work with OEA is most widely presented in the world literature.

Table indicates the some formulas and basic properties of OEA which have been used in the paper. As can be seen, the application of OEA assumes wide variations in functionality, in the nature and length of the oligomer block, in viscosity and so on.

No.	OEA		F	η,cp	Mol.Wt.
1	Tetramethylene-α,ω-dimethacrylate	$M-O-(CH_2)_4-O-M$	4	4,7	226
2	Trioxiethylene-α,ω-dimethacrylate	$M-O-(CH_2CH_2O)_3-M$	4	7,9	286
3	α,ω-Methacryl-bis-ethyleneglycol-phtalate	$C-O(CH_2CH_2O)_n-M$, $n=1$	4	40	390
4	α,ω-Methacryl-bis-tri-ethyleneglycol-phtalate	$C-O(CH_2CH_2O)_n-M$, $n=3$	4	130,5	566
5	α,ω-Dimethakryl-(1,3)-(bis-glycerol)-2-phtalate	(structure)	8	1815	586
6	α-Trimethacryl-ω-methacrylpentaerythritol-dimethacrylpentaerithritol-(dimethacrylpentaerythritol)-adipate	(structure) $n=1$	12	11.10^3	788
7	α-Trimethacryl-ω-methacrylpentaerythritol-dimethacrylpentaerythritol-di(dimethacrylpentaerythritol)-adipate	(structure) $n=2$; $M=\sim C-C=CH_2$ with O and CH_3	16	19.10^3	1172

The purpose of this paper is to illustrate the recent achievements in the field of the OEA polymer modification in the framework of the diagram considered above (Fig. 1).

Compatibity and phase equilibrium

Polymer-oligomer mixtures are, as a rule, thermodynamically incompatible, since they are not capable to form stable one-phase systems at any ratio of components.

Thermodynamic incompatibility and high viscosity of polymer-oligomer compositions predetermine nonequilibrity and "kinetic" nature of their properties. However, not each of the recorded properties (naturally in the framework of accuracy of the experiment and measurement conditions) responds to the degree of the system withdrawal from the equilibrium state. For instance, as has been shown in papers (42, 43), the holdup time of the mixture of cis-polyisoprene with tri-oxyethylene , -dimethacrylate for 30 days at a room temperature does not affect its rheological properties. On the other hand, it is possible to change the character of the concentration dependence of system viscosity by reasoning the composition at a high temperature (44).

The kinetics of the PO chemical transformations in a polymeric medium is particularly sensible to the time prehistory (74). This indicates that polymer-oligomer compositions are in a nonequilibrium state. Consequently,

there arises a new problem, which has not been practically studied as yet, the equilibrium state in viscoliquid polymer-oligomer media.

In a number of papers a certain relationship between the chemical nature of components and different characteristics defining the compatibility limits has been observed.

It has been established, for instance, that the wider the branching of the PO molecules, the higher the value of the Huggins constant for the component data (45). It has been obtained that the more polymer and oligomer differ in polarity, or the more the oligomer block length is, the less are the concentrations which cause the inflection of the "optical characteristics of the mixture - oligomer concentration" curve (15). Polar rubbers are shown to swell better in OEA than nonpolar ones (45, 48). These data, however, do not allow us to estimate quantitatively solubility limits in such systems and to relate them with structure parameters and physical-chemical properties of the composition.

The results of research performed on the mixture of polyisoprene rubber SKI-3 and butadiene-acrylonitrile rubber SKN-18 with α, ω-dimethacrylate by the method of sorption show (50) that the free energies of mixing (Δg_x) under definite values of the component relations change signs, become positive, and, consequently, the system with such concentrations of oligomer becomes heterogeneous (Fig. 2).
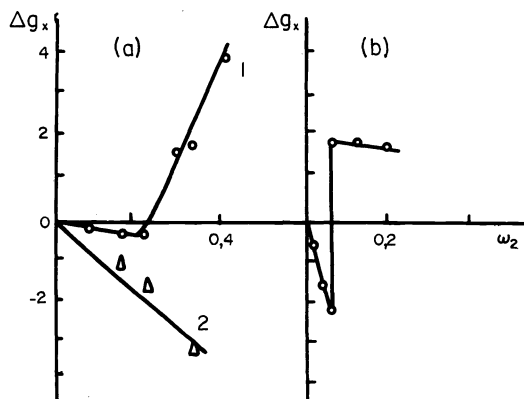

Fig. 2. Concentration dependence of mixing free-energy (Δg_x) for tri-(oxyethylene) -α,ω-dimethacrylate/rubber systems: (a) butadiene-acrylonitrile rubber: SKN-18(1), SKN-26(2); (b) isoprene rubber

A detailed investigation conducted by the microinterference method of compatibility of some flexible- and stiff-chain polymers with oligomers: n-alkanes, n-methylene-dimethacrylates, n-oxyethylene-dimethacrylates and corresponding glycols has shown (51-52) that the phase state of the system depends first of all on the nature of the functional group. For instance, oxyethylene glycols with n = 2 - 13 do not coincide with the investigated polymers (polyisoprene, butadiene-nitrile rubbers, PVC), and oxyethylene-dimethylacrylates turned out to be partially consistent. The upper critical temperatures of solution (UCTS) and asymmetry in the component concentration are typical of the phase state diagrams for all these systems. The positions of binodals change depending on the oligomer molecular mass, on the nature of the oligomer block, on the polymer polarity (Fig. 3).

Fig. 4. presents diagrams of states of cis-polyisoprene with "n"-alkanes and "n"-methylene-α, ω-dimethylacrylates in the form of peculiar binodals. Usual dependence is observed for the non-polar component mixture (35), a decrease in solubility with increasing the oligomer polymerization rate, and for a mixture of the components, differing in polarity, a paradoxical situation takes place - with an increase in the length of the methylene block in the OEA chain, i.e., with increasing the oligomer molecular mass, the areas of the total component compatibility also grow.
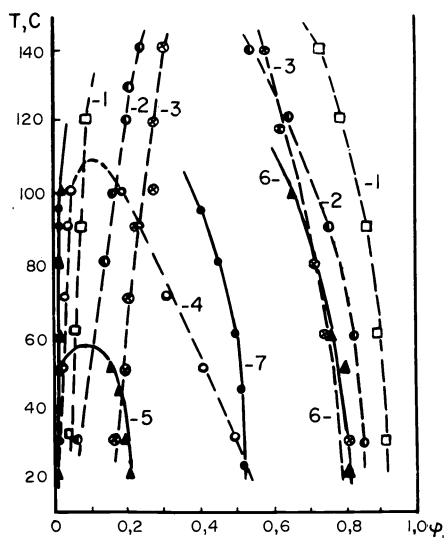
Fig. 3. Phase diagrams for OEA/rubber systems: 1-4 - cis-polyisoprene; 5, 6 - SKN-26; 7 - SKN-40; 1 - OEA-3; 2 - OEA-5; 3 - OEA-4; 4 - OEA-1; 5 - OEA-2 (cf. table I); 6, 7-13 - oxyethylene-α,ω-dimethacrylate
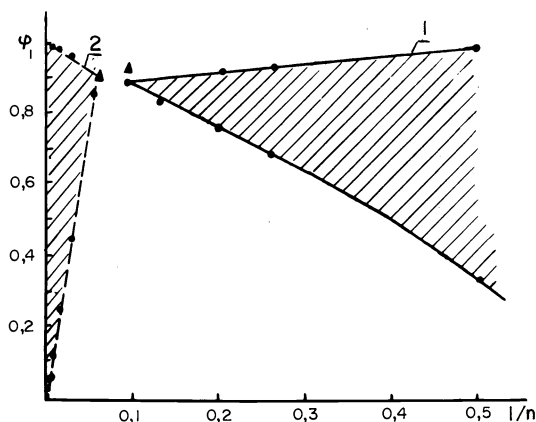
Fig. 4. Phase diagram of cis-polyisoprene compounded with n-methylene-α,ω-dimetha-crylates (1) and n-alkanes (2) at 50°C:
● - observed; ▲ - calculated

This effect turned out to be typical only for the oligomers whose oligomer block and end groups differed in nature. Apparently in such a way the system "compensates" the contribution of polar methacryl end groups to the interaction parameter χ . In the framework of the Flory-Huggins-Scott theory with allowance made for additive contribution of recurrent chains and separate fragments of molecule (according to Van-Krevelen (54)) to the solubility parameters the empirical dependence has been obtained:

$$I/X_I = 67,2 \ (V/RT)(10 + n/8 + n)^2(\varphi'_1 - \varphi''_1)$$

where φ'_1 and φ''_1 are the limiting solubilities (volume fractions) of oligomers with the rate of polymerization X_I and polymer, respectively, V is the molar volume of a monometric chain, and n is the number of units of the oligomer block. This oligomer block length, with which the polar end groups do not affect the compatibility of components.

While analyzing the data on solubility of polymer-oligomer systems it should be stressed that the methods applied by different authors for estimating the limits of the component compatibility do not always provide unambiguous results, since each method has its limits. For instance, the values of critical concentration (C_{cr}) at which the system becomes heterogeneous, for the cis-polybutadiene (SKD) α,ω -dimethacrylate-bis-triethyleneglycol-(phthalate) mixture, obtained by measurement of ptical density (46, 47) and by interference method (52), coincide but differ from the C_{cr} obtained by swelling (48). The temperature dependences of C_{cr} also differ.

Regulation of phase equilibrium conditions is of great practical importance. It has been shown recently that the component compatibility can be varied by small additions of detergents (56). On introducing 1-2% of nonionogenic detergent the value of the limiting swelling of nonpolar rubbers in OEA does not change practically (Fig. 5), but C_{cr} determined from the system optical density (Fig. 6) increases by 2-3 times. This exterior contradiction resulting from the comparison of the experimental data (Figs. 5 and 6) can be easily eliminated with regard to the following facts: 1) usual optical methods "by transillumination" record the particles of >1000 Å in diameter, 2) in the presence of a detergent the surface tension in these systems decreases (96). Therefore, one may assume that with conservation of the total amount of OEA in polymer in the presence of detergents, the latter, diminishing the surface tension at the oligomer-polymer interface,
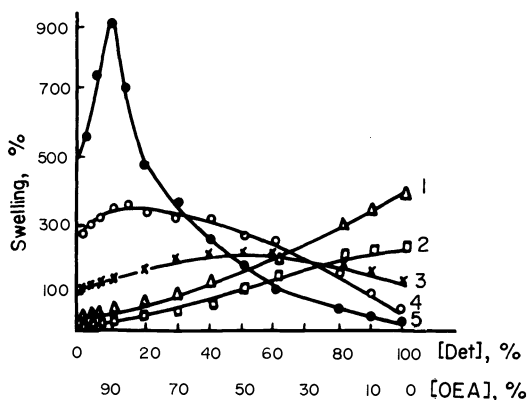
Fig. 5. Influence of OEA-2/
/detergent ratio on the ulti-
mate swelling value of poly-
isoprene (1), cis-polybuta-
diene (2) and butadiene-acry-
lonitrite copolymers SKN-18
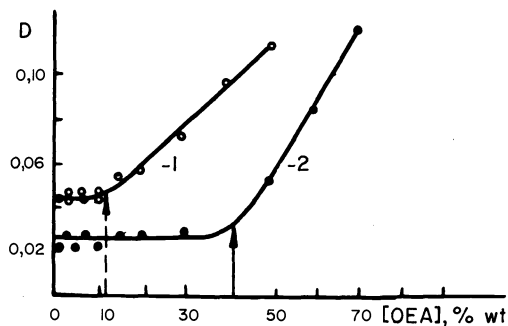(3), SKN-26 (4), CKN-40 (5)

Fig. 6. Optical density (D)
of cis-polyisoprene/OEA-6
system v.s. OEA content in the
presence (1) and absence (2)
of detergent

favour a decrease of the particle dimension of the liquid phase and influ-
ence its distribution in a unit volume of the polymer, i.e., a purely col-
loidal effect takes place. Whereas the change in the particle dimension
leads, as is known, to the change of physical-mechanical characteristics
(35, 47).

Rheological properties

Until recently the viscosity of the polymer–oligomer mixture has been consi-
dered to decrease directly with the amount of liquid component, and the low-
molecular and oligomer plasticizers have not been assumed to differ in ac-
tion (57, 58).

The investigation of rheology of polymer–oligomer mixtures in a wide range
of velocities ($lg\dot\gamma$) and tensions ($lg\tau$) of the displacement shows that the
process of flowing of such compositions is much more complicated, than this
is presented in (57), and is much defined by specific characteristics of the
oligomer component.

The character of the viscosity variation of such systems depends on $\dot\gamma$ and τ,
on the OEA nature and concentration, on the polymer molecular mass, on the
time and temperature prehistory of the system.

Most completely investigated is the rheological behaviour of mixtures of
cis-polyisoprene and cis-polybutadiene with OEA with different structures
(42–44, 59–64). As can be seen from Fig. 7 the branched OEA exert only a
plastizing action upon cis-polyisoprene in the whole range of concentrations
investigated and in a wide range of τ.

Unusual dependences are observed for linear oligomers (Fig. 7). For them in
a mixture with nonpolar rubbers there are three conditional regions of con-
centrations where their influence upon the elastomer–oligomer system visco-
sity is different. With OEA doses 0.5-1.0% η_{ef} increases. In the range of
1.5-3.0% (the range depends on the OEA and polymer nature, on the method of
obtaining a sample, on the test temperature and so on) the mixture viscosity
drastically decreases and, at least, with further increase of the oligomer
dose viscosity monotonously decreases with the OEA concentration.

Such an unusual character of the elastomer viscosity dependence on the liquid
oligomer concentration is observed for different groups of polydispersed
polybutadiene and polyisoprene. An unexpected growth of viscosity in these
experiments is of greatest interest. The ralative value of the effect $K_A =$
$= \eta_n/\eta_o$, where η_o and η_n are the effective viscosity of the initial
rubber and that in the presence of the predetermined amount of OEA, respec-
tively, depends on the compatibility of components, on the rubber MMD, on
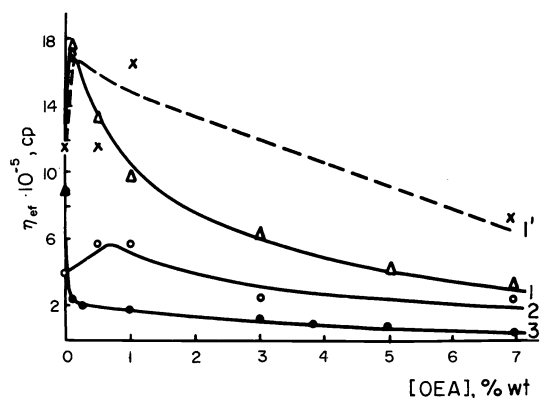the temperature and shift regimes of the experiment and so on (55).

Fig. 7. Concentration dependence of η_{ef} for cis-polyisoprene/OEA mix at 110°C and $\lg \tau = 4.9$ N/sq.m:
1, 1' - OEA-2; 2 - OEA-5; 3 - OEA-7 (cf. table I)
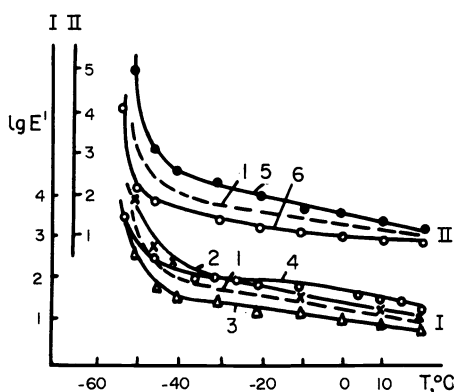1-3 - sample preparation by calendering; 1' - from solution

Fig. 8. Temperature dependence of $\lg E'$ (compressive modulus) for cis-polyisoprene (1) and its compounds with n-oxyethylene-α, ω-dimethacrylates at n = 1 (2, 3), 2 (4), 3 (5, 6).
OEA content: 0.1 (2, 5) and 0.3 (6) % wt, respectively

The natural supposition that the anomalous growth of the mixture viscosity on introducing a liquid PO into viscous rubber is the consequence of the chemical interaction of components which, in principle, may take place in the process of mixing and flowing the composition, has been experimentally verified and rejected (61).

This phenomenon has been hypothetically explained (61, 73) in colloidal-chemical terms in the framework of the Frenkel-Eyring theory. It should be stressed that the antiplasicization effect, which for the last ten years has been a matter of great interest to researchers in all the worls (see, for instance (43, 77, 83)), has been first discovered for a visco-liquid state of polymers in the series of experiments mentioned above. Moreover, while studying the relaxation behaviour of polymer-oligomer mixtures in a wide temperature range by dielectric and mechanical methods (71), it has been shown that one and the same system can be antiplasticized both in glass-like and in highly-elastic states (Fig. 8). It is supposed that the observed retardation of segmental motions in polymer-oligomer systems may be the result of different phenomena - solvation of oligomer molecules by macrochains and (or) a decrease in the free volume, and compaction of molecular packing of the system and so on.

From the above complex of the experimental data two conclusions seem to be most general:

1) one and the same substance, linear oligoesteracrylate, depending on concentration, causes manifestation of three different mechanisms of polymer plasticization known at present as "antiplasticization", "interstructural (interbundle) plasticization" and plasticization itself;

2) antiplasticization can be displayed in glass-like, highly-elastic and viscoliquid states.

The peculiarity observed in the oligomer compound action seems to be important for realizing in practice the oligomer-polymer modification method. For instance, the mixtures of linear and branched OEA display nonadditivity of properties (59), which made it assume "synergims" of the oligomer action.

Specific properties of an oligomer state, in particular, a tendency of OEA for association and formation of structure-arranged regions in a liquid state (25, 28), are displayed when employing mixtures of oligomer and low-molecular plasticizers (62, 65). For instance, as small γ the vescosity of the triple system PCV - OEA-dioctylphthalate (DOP) varies antibately with the

OEA viscosity, and at high γ , when the above-molecular oligomer structure in disturbed, the viscosity of the system is proportional to the viscosity of a liquid phase (Fig. 9).
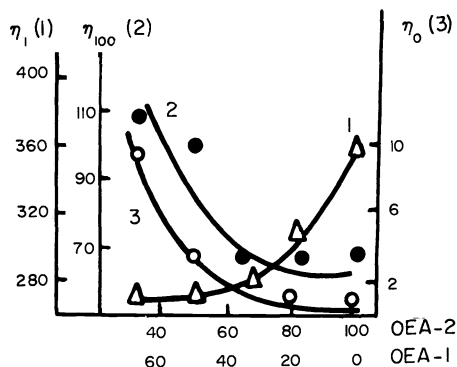

Fig. 9. Influence of OEA-2/OEA-7 ratio on the η_1 (1) and η_{100} (2) of PVC/OEA/DOP plastisol system and on η_0 (3) of plasticizer mixture η_1 and η_{100} are viscosity numbers measured at γ = 1 and γ = 100 sec^{-1}, respectively

The structural association of oligomers causing thixotropy, aside from OEA, is also typical for oligouretanes (66), oligouretaneepoxies (67) and for other structural-regular oligomers.

On the mechanism of PO transform in a polymer medium
The PO polymerization kinetics is not yet practically studied (68, 69).

The absence of systematic investigations on the PO polymerization kinetics in highly-viscous media is apparently connected with the experimental difficulties arising when attempts are made to take account of the nonequilibrium character of polymer-oligomer systems.

Fig. 10 (74) presents kinetic curves of the α , ω -dimethacrylatebutyleneglycol polymerization in polyisoprene medium with different exposure times (the time was recorded from the moment of production until the polymerization beginning). Samples were obtained by the limiting swelling of rubber in OEA (for six hours at a normal temperature) and were stored under conditions of a limited oxygen access. It can be seen that the initial velocities (V_0) and transformation depths (α) first grow, and then (approximately in 10-15 days) reach the limiting value.

However, in case the samples are stored for 30 days (therefore, the kinetic characteristics are not already sensitive to the time prehistory), and then dipped again into OEA for 6 hours (naturally, the weight of the sample is not changed, since it has been obtained earlier by limiting swelling, and for the time of storing no sweating has been observed), the character of kinetic curves is defined not by the total holding time (30 days plus additional exposure time), but only by the time counted off the reiterative swelling, and it coincides with the initial one.

Probably in the process of the polymer-oligomer mixture storing there occurs redistribution of the disperse liquid phase of OEA in a polymer. The OEA particles, having tendency to agglomeration, enlarge and for 10 days the system achieves a quasiequilibrium state, and when the external conditions change, for instance, the sample is again placed in a liquid OEA or when temperature is changed, the equilibrium displaces again. This viewpoint can be proved by the experimental data obtained by Barier et al (32). They have shown (Fig. 11) that in the tetra (oxyethylene)-α, ω-dimethacrylate-PVC system, as temperature elevates from 20 to 90°C, the equilibrium adsorption increases from 7 to 60%, but with decreasing temperature in the opposite course description is almost negligible: only 5-8% of the liquid phase is lost. Consequently, variation of the external conditions (for instance, a decrease in temperature) for equilibrium polymer-oligomer systems does not lead to syneresis of a liquid, which is usually observed in jellies (70), but only the disperse phase is redistributed in dimensions in a polymer
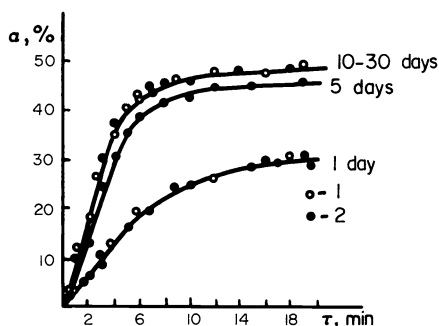
Fig. 10. Kinetics curves of "OEA/cis-polyisoprene matrix" polymerization at 107°C and various exposure times. Samples were prepared by swelling of the rubber in OEA at 20°C till ultimate weight gain (36.5% vol. , over 6 h):
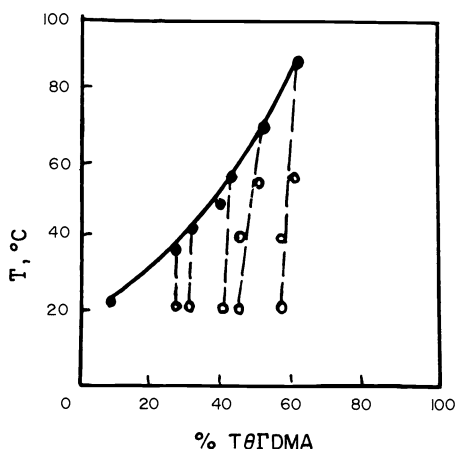1 - first swelling; 2 - re-swelling after 30 days exposure

Fig. 11. Temperature dependence of adsorbtion (●) and desorbtion (o) of tetraoxyethylene dimethacrylate on the PVC

volume. While investigating polymerization of α, ω -dimethacrylate-bis-(triethyleneglycol) phthalate in the matrix of cis-polyisoprene induced by azo-bis-butyronitrile of isobutyric acid (ABN), the original velocities of polymerization have been shown to increase with the OEA in the mixture. It is interesting to note that with an increase of the OEA concentration the E_{ef} decrease and approach the value of E_{ef} of the OEA block-polymerization (55). This makes it possible to suppose that in this system under conditions investigated an increase of the phase stratification facilitates the OEA polymerization. The role of an initiator of the PO polymerization in polymer media is rather essential (80). As follows from the data shown in Fig. 12, the effective constant of the OEA transformation rate in the butadiene-nitrile rubber medium changes by several orders of magnitude as a result of substitution of initiating systems, as Altax or of Altax-dithiomorpholine mixture with, e.g., dicumyl peroxide or hexachlor-p-xylene.

It should be noted that inhibitors of radical processes (for instance, Neozone D) diminish the OEA polymerization rate. This refers both to peroxide and to non-peroxide types of initiators (79, 80).

The data presented are certainly insufficient for correct generalizations. They indicate only the fact the concepts of the mechanism of the process formulated in (25, 58, 79) require additional substantiations and probably elucidations. The following should be taken into account:

1) polymerization kinetics depends on the degree of the system withdrawal from the state of equilibrium (28, 74);

2) rates and depths of the PO polymerization depend on the nature of the components, their relation and on the conditions of the process realization. They may be higher or lower than those in the block-polymerization (64);

3) Chemical interaction of components (copolymerization) may take place or none of it may occur;

4) Chemical transformations of OEA in polymer media may be apparently realized through the stage of β -polymer (or β -copolymer) (25, 28, 30, 31);
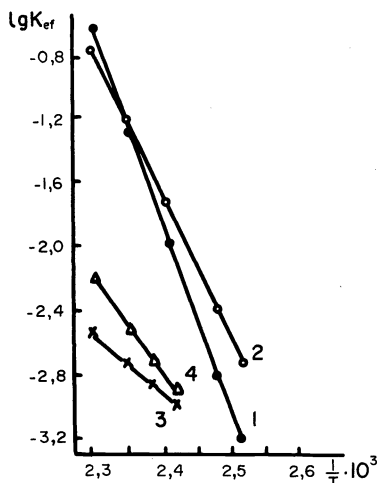
Fig. 12. Temperature dependence of effective rate constant
of OEA-2 conversion (K_{ef}) during SKN-26 matrix polymeriza-
tion in the presence of various initiators (OEA content
30% wt):
1 - dicumyl peroxide (0.5% wt); 2 - paraxylol hexachloride
(0.75% wt); 3 - atlax (6.0% wt); 4 - atlax (4.0% wt) + dit-
hiomorpholine (2.0% wt)

5) the field of molecular forces acting at the polymer-oligomer interface may
produce an orientation effect on the liquid phase and conduce thus the struc-
ture arrangement of the cured system (62, 82).

In the last few years many papers have been published in which the proper-
ties of polymer-oligomer systems cured by different initiation methods are
considered. The problems of radiation initiation of rubber-oligomer systems
are studied in detail in monograph (72).

In chemical initiation employed are organic (7) and inorganic (41) peroxides,
peroxide rubbers (58), oligomer mono- and semifunctional peroxides (92), ac-
tivators of sulfur vulcanization (81), metal salts and oxides (45, 80) and
so on.

Though the ideas on the mechanism of transformations in polymer-oligomer
systems remain controversial, one may assume the following diagram of the
processes in action. When in the primary polymer there are reaction groups
or atoms participating in the kinetic chain transfer, two limiting versions
are possible: a) under condition of the component molecular distribution PO
serves for transverse cross-linking forming a sparse vulcanization lattice
(very much incredible case); b) three-dimensional graft copolymerization
takes place: an aggregate of a cross-linking homopolymer is chemically con-
nected (by one or several bonds) with the polymer matrix.

When a linear polymer has no active centres participating in the chain trans-
fer, the following limiting versions are possible: a) a cross-linked homo-
polymer synthesized in the process of initiated polymerization serves as an
inactive or slightly active filler; b) a cross-linked homopolymer immobili-
zes macromolecules of a linear high polymer and a clathratized structure of
the "snake in a cage" type is formed, or, if the polymer is cross-linked
independently, it is "net in a net" type. Some fragments of the structures
formed are presented in Fig. 13. In real systems all types of processes are
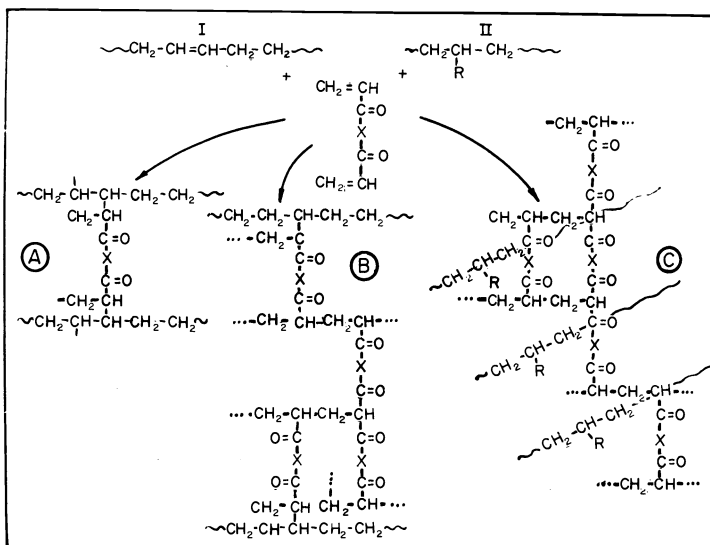likely to realize. Their relation depends on particular conditions.

Fig. 13. A number of OEA transformations which are possible
in reactive (1) and inactive (2) polymer matrix:
A - cross-linking; B - three-dimensional graft polymeriza-
tion; C - "snake in the cage" structure; X - oligomer block

Structure of polymer-oligomer composites

It may be taken proved (27, 29, 35) that cured polymer-oligomer composites
are licroheterogeneous systems with cross-linked polymers serving as a dis-
perse phase. Though the processes of the component mixing and their curing
often proceed under different conditions (and, of source, it should affect
system equilibrium), fast PO gelation fixes the particle distribution laid
in a visco-liquid blank. Dimensions of disperse particles in such systems
and their distribution have been determined by the methods of optical, elec-
tron and X-ray spectroscopy (46-48). A comparison of distribution in visco-
liquid and cured composites shows that it does not change significantly in
polymerization (48).

The investigation of the structure of the radiation-cured PVC-tetra (oxy-
ethylene) α ,ω -dimethacrylate mixture made it possible (32) to reveal
multiple transitions of tg (mechanical losses) and refer them both to in-
dividual PVC and poly-(OEA) structures, and to intermediate PVC microphases,
enriched with poly-(OEA) and to microphases of the three-dimensional poly-
esteracrylate containing PVC.

The influence of polymer on the cured OEA structure and also of oligomer on
the polymer phase structure was discovered.

The IR-spectral examination of gel-fractions of the cured PVC-OEA-DOP system
shows (62) that in the presence of a polymer matrix an interplanar inter-
action of oligomer of oligoether blocks takes place which leads to an addi-
tional ordering of the composite structure fixed by polymerization. More-
over, very interesting data have obtained in (62, 80, 82). X-ray diffraction
patterns bear evidence of the fact that as a result of the OEA curing in the
PVC matrix, long-range order elements appear in the system which are present
neither in the initial products, not in cured ones and nor in their mechani-
cal mixtures (62).

The results of electron-microscopic investigations of the amorphous butadi-
ene-nitrile rubber structure have shown that industrial of OEA into them and
subsequent cross-linking results in the formation of the spheroidal and fib-
rillar type supermolecular aggregates (80).

If the above experimentalldata are proved to be valid for other systems,
this will indicate unambiguously that ir is possible to reorganize the poly-
mer structure in the process of modification and its fixation by three-di-
mensional polymerization.

In the last few years some papers have been published which indicate a pos-
sibility of regulating the structure of polymer-oligomer systems at a super-
molecular level by magnetic force fields in the process of curing or by us-
ing additives of reactive SAC (82).

Properties of cured polymer-oligomer systems

Apparently, the main advantage of the "time plasticization" principle over
other methods of modification of polymer systems consists in the fact that
it allows simultaneous realization of several types of chemical modifica-
tion: to coincide block-polymerization with cross-linking and filling. In
this case the filler is introduced not a priori, but it is synthesized in
the process of the system chemical transformations. The formation of finely-
dispersed cross-linked aggregates bound by covalent bonds with a polymer
substrate allows production of materials with a complex of properties which
can be achieved by no other approaches, or it is very difficult to do it.
For instance, on the basis of the "time plasticization" principle heat-
resistance rubbers have been obtained which combine low hysteresis losses
and high moduli, elevated hardness with strength and endurance to dynamic
alternating loads. This can be explained by the fact that an active filler
chemically bound with rubber strengthens the system and decelerates the de-
structuve processes which take place under deformation. Elastic polyether
bonds favour fast relaxation of a growing gap overload at the top, when it
meets a cross-linked filler particle, and decrease heat build-up in the
fatigue process.

The number of transverse cross-linkings, microphase structure, strength and
the character of bonds at the polymer-"filler" interface and so on can be
regulated by varying the oligomer chemical structure, in particular, the
number of reactive centers, the length and the nature of the oligomer block.

If the account is taken of the diversity of PO structures and the following
from this fact practically unlimited possibilities of modifying the pro-
perties of a polymer material, then there evidently arises a necessity of
development of a substantiated approach to the choice of components.

In this connection it would be very much useful to consider the polymer-
oligomer systems in terms of the colloidal chemistry. Recently such an ap-
proach has been successfully developed as applied to polymer-polymer mix-
tures (75) and to metal alloys. The concept on the extreme variation of pro-
perties in the system transfer from a homogeneous state to a heterogeneous
one has been substantiated for limitedly compatible polymer-oligomer sys-
tems (28, 46, 59).
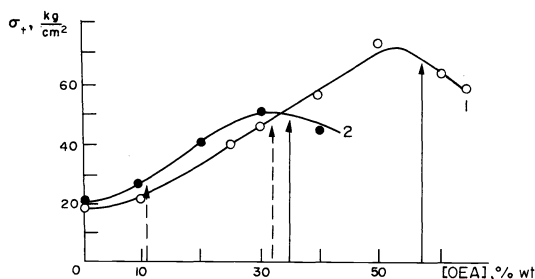
Fig. 14. σ_t versus OEA content for SKD vulcanizates:
1 - SKD + OEA-4; 2 - SKD + OEA-7;
C_{cr} values at 20°C are denoted by dotted line, solid line
corresponds to 150°C (vulcanization temperature)

Fig. 14 illustrates the extreme variation of the concentration dependence of
the polybutadiene strength (σ_p) modified by OEA of different nature. The
maximum values of σ_p practically coincide with C_{cr} of the corresponding oli-
gomers in rubber at the vulcanization temperature. A comparison of the con-

Fig. 15. Influence of OEA content on the mechanical properties $1/Q$ (a), M_{300} (b) and σ_t (c) of SKN-26 vulcanizates loaded with various fillers (45% wt):
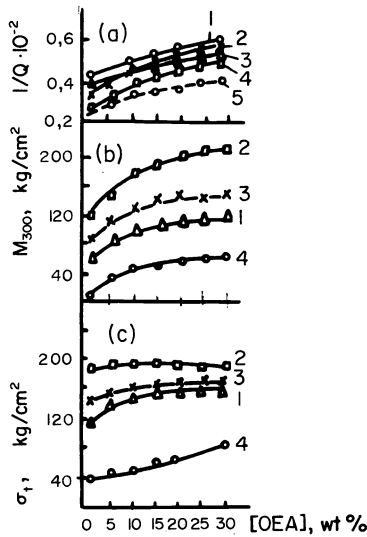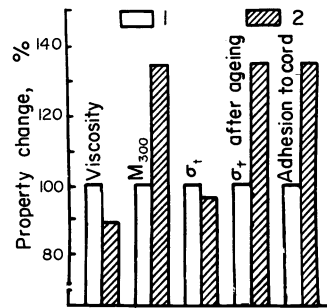1 (SiO$_2$; 2 - carbon black DG-100; 3 - carbon black PM-15; 4 - chalk; 5 - no filler

Fig. 16. Some comparable characteristics of commercial rubber compounds based on nonpolar rubber (1) and of OEA modified rubber (2)

in OEA slows down vulcanization and reduces the density of space cross-linking (58). Neozone D produces an inhibitory effect on the graft polymerization process only if the reaction is initiated by dicumyl peroxide. The initiator of the non-peroxide type (ABN, for instance) does no show any effect of an inhibitor (68). The tradirional inhibitors used for stabilization of tyre rubbers (4010 A type, ED quinol) have been shown to decrease somehow the values of M300 ($\sim$by 10-15%) for rubbers modified by OEA, advance their relative and residual extension ($\sim$15-20%), but increase by 1.5-2 times the resistance to fatigue strength. This experimental fact proves the supposition (see in the foregoing) on the role of the microphase structure in the formation of the system properties.

In the last few years there appear papers in which the method of coefficient planning of the experiment is used for determining the optimum doses of different ingredients in multicomponent systems with PO.

For instance, in (84) variation of three factors is used (dosing of peroximon, Atlax) for developing the prescribing of rubber of the basis of chloroprene rubber which surpasses qualitatively by its technological and physical-mechanical properties the rubber without OEA, in which semiactive carbon black PGM-33 and reserpine being employed.

Fig. 16 shows comparative characteristics of one of the standard tyre rubber recipe based on a mixture of raw rubbers (SKD + BSK + SKI) and a rubber, similar to the former in composition and containing OEA, but corrected by the method of factor experiment (by varying six variables: dosing of sulfur, activator, initiator, filler, plasticizer and OEA). The complex of properties of the modified rubber is much better. Also such an important operation factor as wearability is improved (55).

Some technological properties of polymer-oligomer systems

1. Polyfunctional OEA in a number of cases turned out to be more efficient than tetrafunctional ones (see Note a) (25, 29, 45). However, due to high

Note a. According to the terminology adopted in (25), the OEA with two double bonds are tetrafunctional, i.e., in the process of polymerization each such multiple bond can give rise to two kinetic chains.

centration dependence with the results of morphological studies provides ground for a consideration that the maximum strength for these systems is achieved at a uniform distribution of polyetheracrylate particles of 0.1-1 μm in size in the polymer matrix. Such a distribution is achieved in the vicinity of the compatibility limit, when system passes from a homophase state to a heterophase one. An increase or a decrease of the oligomer concentration in mixture results in variation of the optimum distribution (it is shown in (47, 48, 76) that the size distribution depending on the nature and concentration of components may vary from 100 Å to 15-20 μm) and in a decrease in strength.

However, this is only one side of the problem. There are other important features which define the properties of polymer-oligomer systems.

As is known (78), the optimum properties of cross-linked systems, in particular, of vulcanizers are achieved by combination of different type bonds, energetically stable transverse bonds defining the single completeness of the cross-linking, and liable bonds promoting resorption of stresses arising with the deformation of system in its local regions.

Apparently in the systems under consideration, particularly, when different PO compounds are used, the necessary complex of carbon-carbon, ether, ester and of other types of bonds is realized, which provides the required properties.

In addition to the above mentioned properties, the structure of the microphase as such is also very essential in the formation of properties of polymer-oligomer systems. So far no straightforward proofs have been developed about the cross-linking regularity effect inside the disperse particle on the properties of cured systems, however, a fast increase of dynamic strength of rubbers containing, besides OEA, monofunctional methacrylate derivatives as a third component (55, 56), furnish grounds to assume that the latter cause partial disintegration of the polyetheracrylate cross-linking. A certain violation of the cross-linking regularity should facilitate under cyclic stress mode resorption of the concentration of stresses. A similar effect is observed when not individual PO, but their compounds containing stiff and flexible oligomer blocks and also oligomer compounds, differing in functionality, are employed as modifiers.

And at last, the supermolecular structure of polymer-oligomer systems formed in the process of curing plays an essential role in the formation of properties of materials. This fact is avidenced by a comparison of the data on the crystallization of rubbers modified by OEA with their strength properties (79), by the results of microscopic studies with fatigue strength (80) and roentgenographic data with relaxation characteristics (62).

Therefore, the colloidal-chemical approach and the account taken for supermolecular organization of the structure formed in the process of curing of polymer-oligomer systems are probably required for predicting their properties.

The influence of the composition ingredients on the properties

The diversity of components employed in real systems and the absence of

systematic investigations in this field make it so far impossible to formulate the general principles of composing recipes for obtaining mixtures with the gives properties.

The attempts, which are known (81), are interesting but they do not display all the complications arising in the systems under consideration.

It is worth mentioning some characteristic features which might be useful for making up some particular mixtures.

Fig. 15 (45) shows the values of σ_p and moduli at the 300% extension (M_{300}) of peroxide vulcanizers of SKN-26 rubber containing OEA and different type fillers. Although the degree of cross-linking increases with growth of OEA content and is independent on the filler nature $_p$ increases with the OEA concentration only in the case of inactive fillers, whereas the growth of M_{300} is independent of the type of a filler.

Fillers significantly affect the rheology of polymer-oligomer systems. For instance, at definite OEA ratios, a filler in triplex systems (SKI-OEA-carbon black), antithixotropy takes place (55).

Very contradictory is the influence of inhibitors on the properties of polymer-oligomer mixtures. An increase inaań inhibitor -hydroquinone) dose

viscosity of semifunctional oligomers there arise certain technological dif-
ficulties connected with transportation of such OEA in pipelines, with dos-
ing, introduction into the mixture and with other processes. Therefore, be-
sides physical and chemical reasons mentioned above, it would be very pro-
mising from the technologucal viewpoint to "dilute" viscous semifunctional
OEA by less viscous tetra- and difunctional oligomers. The first papers in
this field turned out to be very prospecting (45). The combinations of OEA
with maleinate oligomers are known to be successfully used for creation of
non-styrol adhesive for glass-plastics (13, 86), and their mixtures with
oligoepoxides and reactive oligodienes for obtaining stable elastomers of
"liquid rubbers" (87). The OEA-maleinate mixtures are also applied for PVC
modification (88).

2. The capacity of OEA to increase noticeably the polymer adhesive proper-
ties is readily employed for producing valuable materials (4, 5, 89, 90).
However, advances "adhesiveness" is not desirable at the stage of component
mixing and formation of polymer-oligomer mixtures. To eliminate these "side"
effects there exist a number of approaches available in literature (91).

3. The diversity of possibilities in principle of initiating the OEA trans-
formation processes has been mentioned above. In practice, however, the
"peroxide" initiation is best widespread. It should be noted that in some
branches of industry introduction of monomer peroxides is not advantageous.
Besides, the required effect is not always achieved with using individual
peroxides (for instance, under conditions of inhibitory polymerization the
peroxide-alternately-valent metal system is applied). And finally, the ac-
tual processes of extrusion, casting, extrusion, colandering, rolling and so
on, in which OEA is used in combination with highly active initiators, can
be fraught with premature cross-linking and with loss of casting properties
of the system. Therefore, even though a number of papers have appeared on
the use of initiators of the non-peroxide type (81), or of oligomer peroxide
(92), it is better to pay attention to the development of systematic inves-
tigations in the field of polyreaction initiation in polymer-oligomer sys-
tems.

4. One of the most omportant virtues of the "time plasticization" principle
is that it does not require any fundamental changes in the designs of mixing
and processing equipment. Moreover, application of this method allows one to
use efficiently the equipment traditional for this field without worsening
the material properties. For instance, it has been shown in (93) that appli-
cation of OEA made it possible to transfer the production of rubber mixtures
on the basis of stiff nitrile rubbers from the method of open mixing (bend-
ing rolls) to that of one-stage enclosed micing. Considerable economy has
been gained both due to intensification of the mixing process and due to
raising the level of manufacturing. The last is another important aspect of
technological advantages of the polymer-oligomer principle. Unfortunately,
there are no serious engineering and economic papers in this fields as yet.

5. Introduction of the "time plasticizer" mixture into the prescribing much
extends the range of polymer compounds for multicomponent mixtures. Poly-
mers of different nature, which have not earlier produced technically valu-
able mixtures, could have been "bound" now thanks to employing PO. It is
this method that has been used for obtaining heat-resistant and wear-resist-
ant covulcanizers of butadiene-nitrile and fluorine-containing rubbers (95,
99), frostproof covulcanizers of fluorine rubber and fluorinesiloxane elasto-
mer (94), oilproof rubbers on the basis of SKEPT and different plastics –
(96, 97, 98) and so on. However, the choice of components and creation of
prescribings are still based on empirical approach and technological experi-
ence.

<div align="center">x   x   x</div>

The modification of high polymers by polymerizable oligomers has thus deve-
loped into an independent scientific trend. Even though the mechanism of
processes and the nature of the property variation in polymer-oligomer sys-
tems are still open to discussion, in the near future one should expect still
advancing development of theoretical and applied work done in this field
which would explain the mechanisms of reactions, create a theory of hetero-
phase three-dimensional copolymerization in nonequilibrium viscous media and
work out new technological procedures of obtaining polymer materials with a
complex of valuable properties.

REFERENCES

1. V.A. Kargin "Modern problems of science of polymers", Moscow Univers. Publishers (1962), L. Trilor "Introduction to the science of polymers" "Mir", Moscow (1973).
2. A.A. Berlin, Avtorskoe svidetel'stvo, USSR № 70736 (1946) (Byulleten' izobretenii № 9 (1949) and № 73031 (1946) (Byull. izobr. № 11, 1949).
3. A.A. Berlin, S.N. Khomyakova, Avt. svid, USSR № 125376 (1949) (Byull. izobr. № 1, 1960).
4. D.A. Kardashov, Khim. nauka i promyshlennost', 5, 602 (1957); "Sinteticheskii klei", Moscow, "Khimiya" (1976).
5. K.I. Dolgopolova et al., Avt. svid. USSR № 254071 (1969), (Byull. izobr. №31, 1969).
6. A.E. Robinson et al., Ind. Eug. Chem., I, № 2, 78 (1962).
7. A.A. Berlin, A.S. Kuz'minskii, S.N. Arkina, Avt. svid. № 411097 (1973) (Byull. izobr., N8 2, 1974).
8. R.Sh. Frenkel' et al., Proizvodstvo shin, RTI i ATI, № 10, 36 (1971).
9. In the collection "Experience exchange of the RTI field plants in application of oligoetheracrylates", Moscow, TsNIITEneftekhim Publishers (1976).
10. English Patent 907432 (1962); United States Patent 3084115 (1963). BRD Patent 1053532 (1956).
11. P.D. Avrasin, in the collection "Glass textolites and other construction plastics", Moscow, Oboronizdat (1960), p. 11.
12. G.D. Andreevskaya, "High-strength orientational glass plastics", Moscow, "Nauka" (1966).
13. G.A. Shtraikhman et al., ZhPKh, 34, № 4, 888 (1961).
14. R.S. Kholodovskaya et al., "Electrotekhnicheskaya promyshlennost'", № 6, 38 (1961).
15. A.A. Berlin, I.Ya. Kaplunov, V.A. Barminov, "Plastics", № 3, 5, (1966).
16. K.P. Belyaeva et al., "Lakokrasochnye materialy i ikh primenenie", No. 6, 5 (1960).
17. E.B. Trostyanskaya et al., "Plastics", № 7, 15 (1962).
18. E.A. Miletkova et al, "Plastics", №11, 10. (1962).
19. Kh.A. Fidler et al., Avt. svid. USSR, 341896 (1971), (Byull. izob. № 19, 1972).
20. V.S. Gorshkov et al., Avt. svid. USSR № 529192 (1976), (Byull. izobr. № 35, 1976).
21. N.E. Sukhareva et al., in the collection "Proceedings of the International Symposium on chemical fibres", Kalinin, "Khimiya" (1974), p. 135.
22. Japanese Patent № 221322 (1969).
23. G. Cowperthwaite, S.P.E. Journal, 29, 59 (1973).
24. S. Yashihashi, Kobunshu Kako, Polymet Appl., 24, № 1, 12 (1976).
25. A.A. Berlin, T.Ya. Kefeli, G.V. Korolev, "Polyetheracrylates", Moscow, "Nauka" (1967).
26. A.A. Berlin, S. Mezhikowskii, Ydeen exacten Wissens, № 10, 626 (1973).
27. A.S. Kuz'minskii, A.A. Berlin, S.N. Arkina, "Uspekhi khimii i fiziki polimerov", Moscow "Khimiya" (1973), p. 239.
28. A.A. Berlin, S.M. Mezhikovskii, ZhVKhO named after Mendeleev, 21, № 5, 531 (1976).
29. A.A. Berlin, Plaste und Kautschuk, № 10, 49 (1971).
30. D. Davis, W. Slichter, Macromolecules, 6, № 5, 728 (1973).
31. W. Salmon, J. Loan, J. Appl. Polymer Sci., 16, 671 (1972).
32. H.E. Bair et al., Macromolecules, 5, № 2, 114 (1972).
33. A.A. Berlin et al., Dokl. Akad. Hauk SSSR, 187, № 6, 1330 (1969).
34. A.G. Shvarts, B.N. Dinzburg, "Consistency of rubbers with plastics and synthetic resins", Moscow, "Khimiya" (1972).
35. Collection "Multicomponent polymer systems", edited by R.F. Gold, Moscow, "Khimiya (1974).
36. S.M. Mezhikovskii, "Nauka i zhizn'", № 4, 118 (1974); S.M. Mezhikovskii, I.K. Churakova "General state and prospects of of development of highly effective process of chemical moulding of products made of oligomers and monomers", Moscow, TsNIITWKhim, (1979).
37. G.N. Petrov et al., "Carbohydrogenoligomers and rubber synthesis on their basis", Moscow, TsNIITEneftekhim (1972).
38. D.B. Boguslavskii et al., "Proceeding of the International Conference on rubbers", Kiev, 1978.
39. L.I. Trepelkova et al., Plastics, № 2, 8 (1972).
40. A. Vasil'ev et al., Caoutchouk and rubber, № 10, 17 (1974).
41. S.S. Ivanchev et al., Avtor. svid. USSR № 451688 (1973) (Byull. izobr. No. 4, 1974).

42. E.I. Vasil'chenko, N.V. Grigorovskaya, R. Sh. Frenkel', I.K. Churakova, Caoutchouc and rubber, № 10, 10 (1976).
43. S. Mezhikovskii, A. Berlin, J. Wassiltshenko et al. Plaste und Kautschuk, № 10 737 (1976).
44. N.N. Schastlivaya et al., "Vysokomolek. soed., 20A, 175 (1978).
45. V.I. Panchenko, Dissertation, VPI, Volgograd (1975).
46. V.N. Kulezney, V.D. Klykova, E.I. Vasil'chenko, A.A. Berlin, S.M. Mezhikovskii, Kolloid. Zh., № 1, 176 (1976).
47. S. Meshikowki et al., Plaste und Kautshuk, № 2, 96 (1977).
48. T.D. Mal'chevskaya et al., Vysokomolek. soed., 18A, № 2, 390 (1976).
49. B.P. Shtarman, "Polyvynilchloride plasticization", Moscow, "Khimiya", (1975).
50. A.A. Tager, S.M. Mezhikovskii, L.V. Adamova, Vysokomolek. soed. (In press).
51. A.E. Chalykh, N.N. Avdeev, A.A. Berlin, S.M. Mezhikovskii, Doklady Akad. Nauk SSSR, № 4, 893 (1978).
52. A.E. Chalykh, S.M. Mezhikovskii, N.N. Avdeev, Vysokomol. soed. (In press).
53. A.B. Kotova et al., Vysokomol. soed. (In press).
54. D.V. Van-Krevelen, "Properties and chemical structures of polymers", Moscow, "Khimiya" (1976).
55. S.M. Mezhikovskii, "Reports on the I-st All-Union Conference on chemistry and physical-chemistry of polymerizable oligomers", (1977), v. II, p. 362.
56. S.M. Mezhikovskii et al., "Proceedings of Symposium "Polymers-77", Varna (1977), p. 37.
57. S.N. Arakina et al., Caoutchouc and rubber, № 10, 12 (1973).
58. A.S. Kuz'minskii, S.M. Kavun, V.P. Kirpichev, "Physical-chemical basis of production, processing and application of elastomers", Moscow, "Khimiya" (1976).
59. S.M. Mezhikovskii et al., Doklady Akad. Nauk SSSR, 229, № 2, 410 (1976).
60. A.A. Berlin, et al., Kolloid. Zh., 38, № 3, 537 (1976).
61. S.M. Mezhikovskii et al., Vysokomol. soed., 19A, № 12, 2719 (1977).
62. S. Meshikowski et al., Plaste und Kautshuk, № 8, 444 (1978); № 10, 566 (1978).
63. S.M. Mezhikovskii et al., "Proceedings of the All-Union Symposium "Theory of mechanical processing of polymer materials", Perm', (1976).
64. S.M. Mezhikovskii et al., "Proceedings of the XI-th Mendeleev Symposium", v. 2, p. 207, "Nauka", Moscow (1974).
65. T.M. Shapiro et al., Vysokomol. soed., 20A, № 2, 420 (1978).
66. Yu. S. Lipatov et al., Vysokomol. soed., 13A, № 11, 2417 (1971); 11A № 6, 1202 (1969).
67. G.K. Romanovskii, Dissertation, VNIISK, Leningrad (1977).
68. S.N. Arkina et al., Vysokomol. soed., 12A, № 6, 1211 (1970).
69. Z.A. Karapetyan et al., Vysokomol. soed., 17A, 1969 (1975).
70. S.P. Papkov, "Geletinous state of polymers", Moscow, "Khimiya" (1974).
71. T.I. Borisova et al., "Vysokomol. soed., 20B, № 12, 900 (1978).
72. F.A. Makhlis, "Radiation chemistry of elastomers", Moscow, Atomizdat (1976).
73. S.M. Mezhikovskii, E.I. Vasil'chenko, A.A. Berlin, "Abstracts of the VII-th All-Union Conference on physico-chemical mechanics", "Nauka i tekhnika", Minsk (1977), p. 197.
74. A.A. Berlin, L.A. Zhiltsov, S.M. Mezhikovskii, Kolloid. Zh., 40, № 3, 545 (1978).
75. V.N. Kulezney, Dissertation, MITKhT, Moscow, 1973.
76. Yu.K. Ovchinnikov et al., Vysokomol. soed., 17A, 616 (1975).
77. P.V. Kozlov, A.V. Efimov, "Encyclopaedia of polymers", v. 2 (1974), p. 627.
78. B.A. Dogadkin, "Chemistry of elastomers", Moscow, "Khimiya" (1974).
79. S.N. Arkina et al., Vysokomol. soed., 16A, № 12, 2695 (1974).
80. R.Sh. Frenkel', Dissertation, MITKhT, Moscow (1979).
81. A.S. Kuz'minskii et al., Caouschouc and rubber, № 12, 5 (1974).
82. R.Sh. Frenkel's et al., "Abstracts of the International Symposium on moleculat chemistry", v. 6, p. 51, Moscow, "Nauka" (1978).
83. P.P. Perepechko, "Introduction to the physics of polymers", Moscow, "Khimiya" (1978).
84. B.B. Gol'dberg et al., "Production of tyres, RTM and ATI", № 8, I, (1975), Tsniiteneftekhim.
85. N.V. Kuronosova et al., Kolloid Zh., 37, № 6, 1174 (1975).
86. I.M. Al'shits et al., Vysokomol. soed., 10B, № 2, 129 (1968).

87. E.B. Khabarova et al., Caoutchouc and rubber, № 3, 45 (1976).
88. V.S. Gorshkov et al., "Plastics" (In press).
89. E.K. Lotakova et al., "Production of tyres, RTI and ATI", № 8, I (1972), TsNIITENeftekhim.
90. V.I. Panchenko et al., Abstracts of "Methods of elevation of polymer adhesion", Moscow, The Mendeleev VKhO (1977), p. 26.
91. A.A. Berlin, V.E. Basin, "Foundations of polymer adhesion", Moscow, "Khimiya" (1974).
92. S.S. Ivanchev et al., DOP AN SSSR, 20, № 12, 1089 (1976).
93. G.A. Baranova et al., Proceedings of the Conference 'Principal trends of increasing the quality of rubbers on the basis applying compatible systems of elastomers", Dnepropetrovsk (1976), p. 69.
94. N.A. Leshchenko, V.S. Evchik, ibid., p. 26.
95. V.A. Egorov et al., ibid. p. 39.
96. R.Sh. Frenkel' et al, ibid., p. 13
97. L.N. Makarova et al. ibid., p. 38.
98. G.I. Maksutov et al., ibid., p. 39.
99. E.S. Yurtseva et al. ,"Caoutchouc and rubber", № 8, 8 (1974).
100. S.N. Arkina et al., "Production of tyres, RTI and ATI," № 7, 3 (1974), TsNIITENeftechim.