THE APPLICATION OF RADIOTHERMOLUMINESCENCE METHOD TO THE ANALYSIS OF POLYMERS AND POLYMER COMPOSITES

V.G.Nikol'skii

Institute of Chemical Physics, USSR Academy of Sciences, 117334 Moscow, USSR

Abstract - The basic results concerning the examination of copolymers,cross-linked polymers and polyblends structure, obtained by means of radiothermoluminescence method, are reviewed. The main emphasis is on the glow curve shape analysis that allows: a) to determine quantitatively the random copolymer composition; b) to reveal the existence of blocks in macromolecules; c) to examine the grafted copolymer distribution in polymer matrix; d) to estimate the degree of cross-linking both for individual polymers and heterogeneous polyblends; e) to study the mutual solubility of polymers.

INTRODUCTION

The luminescence phenomenon, observed while heating a solid substance, preliminary exposed at low temperatures to any type of penetrating radiation (gamma-rays, electrons, X-rays, and so on) is called radiothermoluminescence. For the first time, this phenomenon was found and examined in inorganic crystals and glasses as far back as the beginning of this century. The investigation of radiothermoluminescence in organic substances was started considerably later. Thus, in 1960, at the Institute of Chemical Physics of the USSR Academy of Sciences, a rather interesting peculiarity of radiothermoluminescence process in organic substances was revealed. It proved that on gradual heating of irradiated crystals, as well as of amorphous substances, occur luminescence flashes at temperatures corresponding to those of structural transitions. The discovery of this relationship leads, finally, to the creation of a new method of organic solids structural analysis - the radiothermoluminescence method (RTL). At present, this method is successfully applied to various problems of organic and polymer chemistry. Thus, it appeared to be useful for examination of copolymers, filled polymers, oriented polymer films and fibres, cross-linking processes and also for estimation of homogeneity degree in bi-and multicomponent mixtures of organic substances. Together with those, the RTL method makes it possible to investigate various physico-chemical processes in irradiated substances such as ions and radical stabilization, charge migration, formation of exited states etc. In the present paper the studies dealing with RTL application to polymers and polymer compounds are reviewed.

BASIC PECULIARITIES OF THE RADIOTHERMOLUMINESCENCE MECHANISM AND THE EXPERIMENTAL TECHNIQUES

The mechanism of radiothermoluminescence of organic solids has been studied by several Soviet investigators (2-11), A.Charlesby et al. (12-15), M.Magat et al.(16-18) and also by some others (19-23). The basic results of these papers are reviewed in detail by R.Partridge (24), V.Vonsjatskii and G.Bojarskii (25). For this reason here we shall summarize only briefly the basic peculiarities of radiothermoluminescence mechanism.
The irradiation of solids, polymer as well, by gamma-rays or electrons results in ionization of molecules. At low temperatures a portion of electrons and positive ions produced this way is stabilized (trapped) in various types of traps. In particular, traps for electrons may be functional groups or single molecules with a positive electron affinity, free radicals and also dielectric cavities, the latter is best pictured as an irregular space bounded by a particular local arrangement of molecular chains.

When heating some irradiated substance, the trapped charges begin to migra-
te, drawing gradually together and, finally, recombine. Ion recombination
leads to formation of neutral exited molecules which return to the ground
state by luminescence emission. In many cases the luminescence process is
due largely not to the molecules of examined substances but to those of
impurities dissolved in this substance acting as luminescence centres.
In most cases the radiothermoluminescence is produced by irradiation of
examined substance at 77 K, using gamma-sources, electron accellerators or
X-ray installations. The heating of irradiated samples is carried out in-
side a thermoluminograph. The principal scheme of this apparatus is given
in Figure 1. A thermoluminograph involves cryostat, monitoring photomultip-
lier and a reservoir filled with liquid nitrogen. After the cryostat is
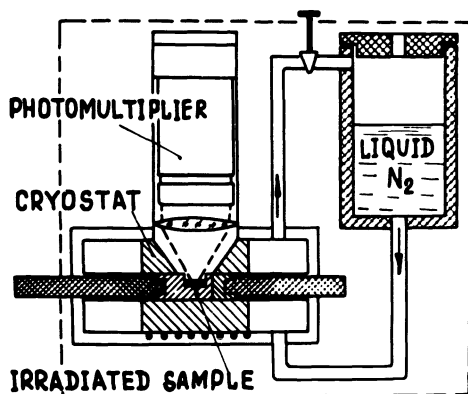

Fig. 1. Schematic representation of the thermoluminograph
        installation.

cooled to 77 K, the stock containing the irradiated sample is placed into
the cryostat, which is then heated smoothly, the glow being recorded by
means of photomultiplier.
As a rule, a part of stabilized charges recombines already at low tempera-
tures due to the beginning of motion of side groups or small segments of
macromolecules in the irradiated sample. The majority of ions recombine,
however, near glass transition point, thus resulting in appearance of the
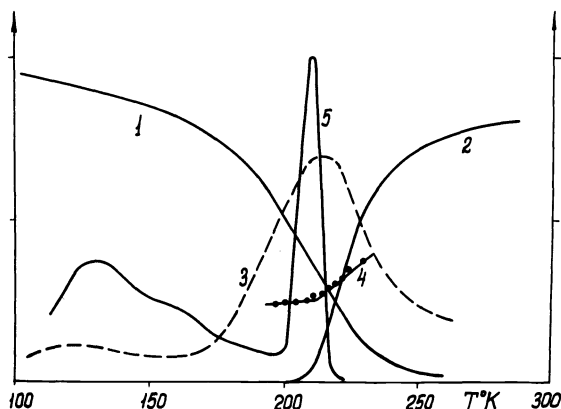

Fig. 2. Results of relaxation transitions study of butadiene/styrene
        random copolymer (styrene 30 wt%): 1 - temperature dependen-
        ce of n.m.r.absorption line width; 2 - temperature dependen-
        ce of deformation amplitude. Frequency 0.01 Hz; 3 - coeffi-
        cient of mechanical losses, measured at a frequency of 0.1 Hz
        3 - coefficient of mechanical losses,measured at a frequency
        of 1.1 Hz versus temperature; 4 - specific volume versus
        temperature; 5 - RTL glow curve.

most intensive RTL maximum. Fig. 2 shows the glow curve, i.e. the dependence of luminescence intensity on temperature for a random styrene-butadiene copolymer (SBC) containing 30 w/w of styrene (curve 5). Here also the results of investigation of molecular relaxation in this copolymer by several other methods are given: the specific volume-temperature dependence (curve 4), that of coefficient of mechanical losses measured at a frequency of 0.1 Hz (curve 3) and so on. The glass transition temperature of the copolymer was found to be equal to 208 K according to dilatometry and 211 K as determined from the position of the intensive RTL maximum in the glow curve. The same was found for a great number of amorphous and semicrystalline polymers; the temperature, corresponding to the most intensive RTL maximum differs from that measured by dilatometric or relaxation means with frequencies of 0.01-0.1 Hz less than 3-5 degrees. The half-width of RTL maxima, observed in glass-transition region are about 5-10 K for amorphous and 15 - 35 K for semicrystalline polymers, respectively.
The activation energy of thermoluminescence, measured in any temperature region, was found to be equal to that of molecular relaxation process, which results in ion recombination in the same temperature region. Due to this fact the analysis of both glow curve shape and RTL maxima position allows calculation of the activation energy of molecular relaxation process by several methods. A detailed review of these methods has been given, for example, by Fleming (21).
One of the most effective methods for obtaining the activation energy value is that of initial rise (8,26). In the initial stage of the glow curve or of individual maximum the thermoluminescence intensity increases with increasing T according to the expression:

$$I\ (T) = A \cdot \exp\left(-\frac{E^*}{kT}\right)$$

where A is a constant and E* is the apparent value of activation energy in a given temperature range. Plotting the logarithm of initial intensity versus reciprocal temperature, it is possible to determine the activation energy value from the curve slope with great accuracy.
It has to be emphasized that the presence of oxygen, carbon dioxide and also some other molecules with rather small dimensions, dissolved in irradiated samples, influences the recombination of stabilized ions. Thus, on heating of irradiated substance containing dissolved oxygen, a portion of ions do recombine at the moment corresponding to the start of oxygen diffusion, i.e. at temperatures 60-90 K lower T_g value. This results in the appearance of an intensive "Oxygen" maximum in the glow curve. This effect is used for measuring the concentration of dissolved oxygen in the study of an oxygen diffusion process and also in some other cases. Nevertheless, in order to study polymer structure, the dissolved gases usually are evacuated from the examined samples.
At low doses (up to 1-3 Mrad) RTL maxima intensity of organic substances increase proportionally to the dose increase; due to this, the glow curve shape remains practically unchanged with the dose increasing. The changes in the glow curve shape begin when the dose exceeds the value of about 1-2 Mrad. For the majority of polymers it is accompanied by decrease in intensity of RTL maximum located in glass transition region, with dose increasing. That is why the common irradiation dose is about 1 Mrad. Thus, all the glow curves, presented in this paper, were obtained for samples evacuated to remove dissolved gases and irradiated up to a dose of 1 Mrad. The radiothermoluminescence intensity of most polymers, excited in mentioned above conditions is rather high. This allows investigation of ly small samples - thin films and individual fibres, whose weight does not exceed tenths or even hundredths part of a milligram. This circumstance substantially broadens the number of potential subjects of investigation. Besides, the use of a small amount of substance allows reduction by several times of the duration of experiment due to the increased heating rate.

THE STUDY OF RANDOM, BLOCK- AND GRAFT COPOLYMERS

The structure and properties of any copolymer depend both on it's chemical composition and distribution of monomer units in macromolecular chains. If the copolymerization of some monomers A and B results in formation of macromolecules with random distribution of monomer units, glass-transition temperature of this copolymer will occupy the intermediate position between T_g's of both homopolymers. The variation in copolymer composition causes the gradual shift of it's glass-transition temperature from that of one homopolymer to the other one.

Let us consider, for example, the dependence of glass-transition point on composition of random copolymer of dimethylsiloxane (DMS) and methyltrifluoropropylsiloxane (M3FPS), shown in Fig.3. The results obtained for vulcanized samples by means of both RTL method and so called linear dilatomet-
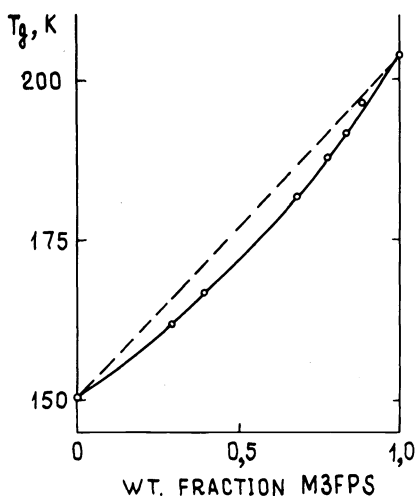

Fig. 3. T_g's values of dimethylsiloxane/methyltrifluoropropylsiloxane copolymer versus the latter comonomer content (wt %).

ry were given in our paper (27). It has been established that the glow curve of all the examined copolymers is characterized by an intensive maximum whose position monotonically changes with the increase in M3FPS content from 150 up to 203 K. Half-width of this maximum does not exceed 12 K whereas it's temperature practically coincides with T_g value, as measured by dilatometry method.
The temperature of a narrow well-resolved RTL maximum can be measured with high accuracy. This allows to determine the copolymer content from the position of RTL maximum, if glass-transition temperature dependence on the copolymer content is known. In particular, for the dimethylsiloxane - methyltrifluoropropylsiloxane copolymer the weight content of both components can be determined by means of RTL method with an accuracy of 1 wt %.
In case the distribution of monomer units in macromolecules differs from the random one, it can reflect in increase of polymer structure heterogeneity. Let us consider in this connection some results, obtained for ethylene-vinyl acetate copolymer by RTL and X-rays means. Samples of this copolymer, prepared by slow cooling of melt, the average rate being about 2.10^{-2} degree/ sec, were investigated in our study (28). It has been found that T_g shifts smoothly with content variation till the ethylene content does not exceed 50 w/w (curve 1 in Fig. 4). The following increase of ethylene content in polymer resulted in formation of individual crystallites. The increase of ethylene content from 50 up to 100 wt % is accompanied by gradual increase in crystallinity degree with the simultaneous widening of RTL maximum, T_g value being practically unchanged.
The occurrence of a horizontal region in the dependence of T_g value versus copolymer composition is, in our opinion due to the formation of crystallites of small groups of ethylene chains segments acting as "physical" cross-links between copolymer molecules; their existance, complicating glass-relaxation process, thus inhibits the possibility of T_g shifting lower than 233 K. To verify this suggestion we have studied thin copolymer films obtained by rapid quenching of melt in liquid nitrogen with rates of 150-300 degree/sec. Quenched samples were irradiated at 77 K by gamma-rays and then studied by RTL. This proved that quenching resulted in a decrease of T_g value of almost 20 K for copolymers with a high ethylene content.
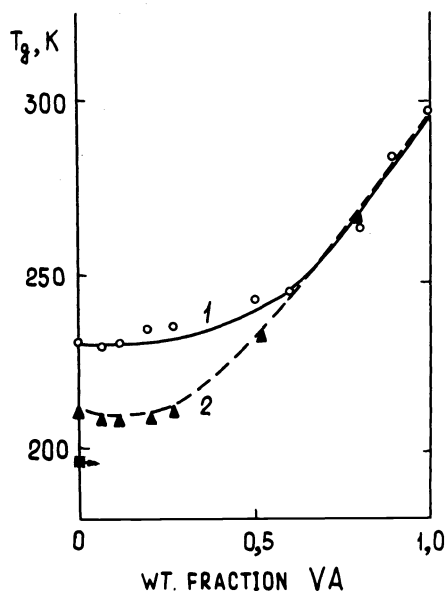
Fig. 4. T_g's values of ethylene/vinyl acetate copolymer versus
         the latter comonomer content (wt %). Samples are pre-
         pared from melt. Cooling rates: 1 - (1 ÷ 3) x 10^{-2}
         degree/sec, 2 - 150 ÷ 300 degree/sec. The symbol ■►
         in ordinate axis indicates the hypothetical T_g value
         (29) of completely amorphous PE.

Dependence of T_g value versus quenched samples composition is also plotted
in Fig. 4 (curve 2). The arrow on the ordinate axis indicates the glass-tran-
sition temperature to be peculiar, as suggested (29), to completely am-
orphous polyethylene. The existance of a small horizontal region in curve
2 is likely associated with the impossibility of obtaining amorphous samp-
les of copolymers with an ethylene content exceeding 80 wt % by quenching
in liquid nitrogen.
The appearance of blocks in molecules of non-crystallized copolymers can
be securely determined by RTL because of it's maxima broadening in glow
curves. Masagutova et al. (30) carried out a comparative study of some
butadiene-styrene copolymers, produced by several firms of USA, Japan etc.
with one and the same styrene content - about 25 wt % . The glow curves
of two of copolymers studied - "Duradene" and "Solprene-1204" are shown
in Fig.5. T_g's values of "Duradene" and "Solprene-1204" were found to be
207 and 216.5 K, respectively. According to IR-spectroscopy the amount of
butadiene units in 1,2 position for the former copolymer is 9.7% (from the
total amount of butadiene units), whereas for the latter this value is
34%.
The amount of styrene units, forming blocks in copolymer molecules has
been determined according to Kolthoff method (31). This value for "Durade-
ne" copolymer was found to be three times smaller by comparison with
"Solprene" and equal to 1.6 and 4.6%, respectively. The latter fact is
likely to be the reason of substantial broadening of the RTL maximum in
"Solprene-1204" copolymer.
Let us consider now the application of RTL method for examination of graft
copolymers. Our studies (32,33) have shown that grafting of various mono-
mers to LDPE films resulted in PE glass-transition temperature increase,
accompanied by substantial decrease of corresponding maximum intensity in
the glow curve. Thus, for example, due to styrene grafting to polyethylene
in amount of about 20-30 wt % PE T_g value increases for 15-20 degrees,
whereas the intensity of RTL maximum, located in glass-transition region,
decreases by 5-20 times. It is to be emphasized that due to these changes
the glow curve of the copolymer strongly differs from that of a polyethyle-
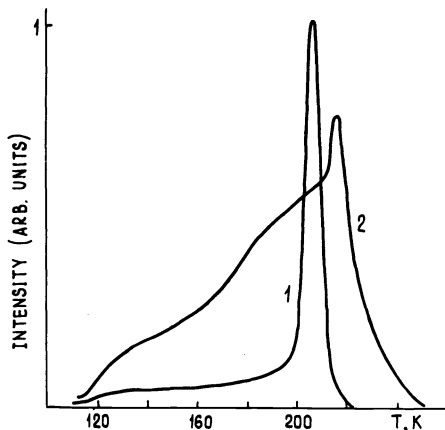ne-polystyrene mechanical mixture.

Fig. 5. Glow curves for styrene/butadiene copolymers: 1 - "Duradene";
2 - "Solprene-1204". Styrene content-25 wt %.

The most pronounced changes in glow curve shape are observed on grafting of monomers to spherulitic high density polyethylene or polypropylene (PP) films. In Fig.6 a glow curve (curve 1) of a thin film of isotactic PP is shown, the average spherulitic size being about 100 μm; the glass-transition temperature is 254 K. The same Figure shows the glow curve of a copolymer, prepared by radiation vapor-phase grafting of styrene to PP film
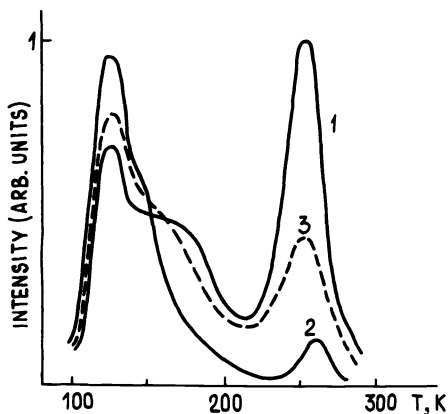

Fig.6. Glow curves: 1 - PP sample, average spherulitic size - 100 μm;
2 - grafted PP sample prepared by radiation-induced vapor-
phase grafting of styrene. Polystyrene content - 5 wt %;
3 - previous sample after annealing at 453 K for 5 hours.

(curve 2). The distribution of grafted product in this case is practically uniform, it's weight content being about 5 wt %. It can be seen that despite the rather small amount of grafted polystyrene, the intensity of a maximum, located in the region of 250-265 K, decreases more than tenfold. At the same time for the copolymer, heat treated at temperatures exceeded that of PP melting point, the intensity of a maximum, located in PP glass-transition region, somewhat increases (curve 3 in Fig.6). After this procedure the grafted polymer could be removed from PP film by means of benzene extraction for several hours. It proved to be that glow curve of heat treated and then subjected to extraction sample little differs from that of the initial sample i.e. from curve 1.

One of possible explanation of observed changes in glow curves of polyole-
fins, caused by grafting, is most likely the tension increase of the mole-
cules and the reduction of free volume value, due to accumulation of
grafted product. This process must complicate the segmental mobility of
polyolefin molecules and, consequently, reduce the recombination rate of
stabilized ions. Apparently, this is the main reason that causes the in-
tensity weakening of basic RTL maximum in a glow curve of grafted copoly-
mer. In any case, the analysis of these curves allows the deduction of useful
information about kinetics of grafting as well as distribution of grafted
polymer inside polyolefin matrix.

STUDY OF VULCANIZATION OF POLYMERS AND POLYMER BLENDS

It is known that the vulcanization process represents formation of a
three-dimensional network by cross-linking of macromolecular chains. The
structure of a network formed this way depends on both the type of cross-
links and the concentration of chains inside the network, i.e. on the
value of $1/M_c$, where M_c is the number-average molecular mass of a chain
fragment between the neighbouring junctions. There are several methods of
M_c determination. For the three-dimensional network, already formed, M_c is
determined from the equilibrium swelling value, strength or modulus values
and also by glass-transition temperature shift.
Vulcanization causes an increase in glass-transition temperature of a poly-
mer with the simultaneous increase of a basic RTL maximum. If the vulca-
nization process has not been accompanied by grafting of any polyfunctional
monomer, M_c value can be determined from the glass-transition temperature
shift according to the following empirical equation (34):

$$M_c = \frac{3,9 \cdot 10^4}{T_g - T_{go}}$$

where T_g is the glass-transition temperature (K) of vulcanized polymer and
T_{go} – that of uncrosslinked one. The given equation was repeatedly used for
description of crosslinked polymers. The sensitivity of RTL method allows
to fix T_g shift for vulcanized polymers even when M_c value does not exceed
$(2 \div 3) \times 10^5$ mole/cm^3.
Fig. 7 shows the T_g shift versus dose value for the radiation vulcanizates
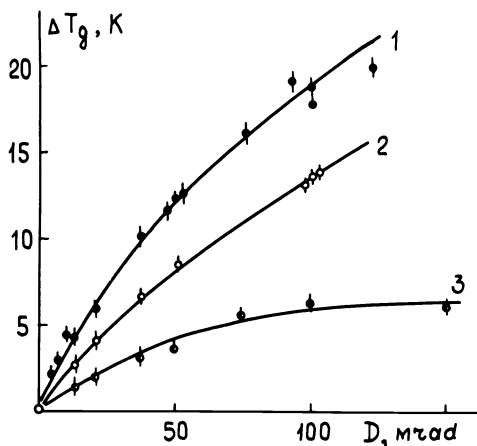

Fig. 7. Glass-transition temperature shift, ΔT_g for polybu-
        tadiene samples (66% of butadiene units in 1,2 – posi-
        tion) vulcanized by irradiation versus dose. Vulcani-
        zation temperature (K): 1 – 300, 2 – 273, 3 – 77.

of polybutadiene as determined by RTL method. Curves 1, 2 and 3 correspond
to polybutadiene samples, vulcanized at 300, 273 and 77 K, respectively.
These results allow to establish (35) that the rate of polybutadiene ra-

diation – induced vulcanization increases with temperature rise, the most noticeable increase in crosslinking rate being observed in the glass-transition temperature range. The concentration of network chain fragments, as determined from a basic RTL maximum shift of radiation vulcanizates of polybutadiene, butadiene-styrene copolymer, natural rubber and of several others, was found to be similar to values obtained by some other methods.

The RTL application proved to be the most valuable one for the examination of heterogeneous polyblends vulcanization (4, 36, 37). It is well known that the vulcanization of a heterogeneous binary polyblend in most cases resulted in formation of heterogeneous system, composed from the regions of one crosslinked polymer and those of the other. For example, the sulfur vulcanization of a blend of cis-polybutadiene with butadiene-nitrile rubber results in formation of heterogeneous rubbers, exhibiting two glass-transition temperatures (38) and, therefore, two vulcanization networks. The concentration of chain fragments in these networks can, in principle, noticeably differ due to nonuniform distribution of sulfur and other ingredients in the initial mixture. Determination of the concentration of chain fragments for any of these networks is possible only when the shifts values of both glass-transition temperatues due to vulcanization process are known.

Fig.8 shows glow curves for cis-polybutadiene and polyisoprene blend, containing 2 wt % of sulfur, before vulcanization (curve 1) and after (curve 2). It can be seen that each curve exhibits two maxima; however,
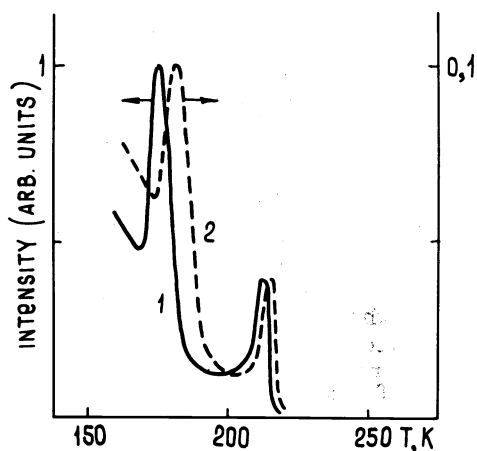

Fig.8. Glow curves for cis-polybutadiene/polyisoprene blend (weight ratio 50:50): 1 – uncrosslined sample, containing 2 wt % of sulfur; 2 – sulfur vulcanized sample.

both maxima, observed in the second curve, are shifted towards higher temperatures. The comparison of curves allowed us to determine the shift values of both T_g's. Using these values the concentration of chain fragments for both networks was calculated by means of equation cited above. These calculations did not reveal any noticeable differences in network densities, indicating thus, the rather uniform distribution of chemically bonded sulfur in vulcanizate structure.

There can be given only few examples of successive preparation of a material with improved homogeneity by vulcanization of a heterogeneous polyblend. For example, it has been found that vulcanizates of polyblends of polybutadiene with butadiene-styrene or butadiene-methylstyrene rubbers, prepared under certain conditions, are characterized by a single maximum of mechanical and dielectrical losses (39), as well as a single intermediate maximum in the RTL curve (36,37). The effect of both temperature and vulcanization technique on structure of a blend composed from butadiene-styrene copolymer ("Eruoprene-1500") and cis-polybutadiene ("cis-Europrene") has been examined in detail by RTL means in our study (37).

Fig. 9 shows glow curves of vulcanizates based on "cis-Europrene"/"Europrene-1500" blend, prepared by radiation crosslinking at 293, 373, 416 and 433 K. For all the examined vulcanizates the average concentration of chain fragments, as determined from the equilibrium modulus values, was much the
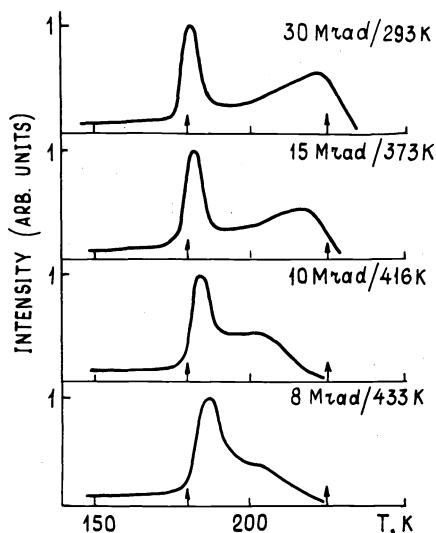
Fig.9. Glow curves for "cis-Europrene"/"Europrene-1500"blend vulca-
        nizaed by irradiation (weight ratio 40:60): a - 30-Mrad,
        293 K; b - 15 Mrad, 373 K; c - 10 Mrad, 416 K; d - 8 Mrad,
        433 K.

same and equal to $5,3 \times 10^5$ mole/cm^3. It can be seen that crosslinking at
room temperature is accompanied by rather weak approach of glow curve maxi-
ma. However, with high-temperature crosslinking at 416 and 433 K the maxima
in the glow curves of vulcanizates were drawn together and superimposed. It
has been established that the formation of such a "pseudo-homogeneous" vul-
canizate takes place only when the vulcanization temperature is high enough
and the average concentration of network chain fragments exceeded $5 \cdot 10^5$
mole/cm^3. The results obtained allowed us to conclude that the examined poly-
blend, being heated, transforms into the more homogeneous state due to
mutual interpenetration of components, the polyblend phase structure being
fixed by three-dimensional network of crosslinks, formed during vulcaniza-
tion.

THE STUDY OF POLYMER BLEND STRUCTURE; MIXING OF POLYMERS
UNDER HIGH PRESSURES

It is well known that in most cases polymers are thermodynamically incompa-
tible between each other. Due to this, their mixing in molten state or in
mutual solvent with its following evaporation, results in formation of
heterogeneous two or multiphase material consisting of microregions or dom-
ains of the initial polymers. If the interaction between distinct phases is
small enough, the binary polyblend shows two glass transition points, coin-
ciding with those of individual components. The increase in interfacial
interaction, as well as their partial solubility is accompanied by gradual
convergence of the glass-transition values of heterogeneous polyblend.
The true compatible polymers, able when mixed to form kinetically stable
and homogeneous blends, possesssing single glass transition value, single
melting point etc. come up very seldom.
Essential is that basic properties of polyblends strongly depend on their
structural characteristics. That is why the developing of methods suitable
for quick and effective analysis of homogeneity, phase structure, the type
of interfacial interaction etc. is a problem of current interest.
As far back as 1965-1967 Goldanskyi, Buben et al. established the following
interesting property of polyblend's thermoluminescence (4). It was found
that the luminescence produced by individual polymer phases proceeds in
heterogeneous systems independently. In particular, in the glow curve of
two-phase polyblends two thermoluminescence maxima are observed located in
glass-transition temperature regions and coinciding in shape with those
of the initial components. The variations in the weight ratios of polyblend
components result only in a gradual increase of the intensity of one

of these maxima with the corresponding weakening of the other one. This
can be illustrated by the mixtures of cis-polybutadiene and ethylene-pro-
pylene copolymer studied in paper (40). Glow curves of these polyblends
are given in Fig.10. It can be seen that decrease of cis-polybutadiene
content is accompanied by gradual decreasing of intensity of the maximum,
located in the temperature region of 172-177 K, whereas its position as
well as those of other maxima remains practically unchanged. T_g values of
this polyblend determined from the positions of maxima in glow curves were
found to be 175 K and 209 K over the whole composition range and coincided
with those of initial pure cis-polybutadiene and ethylene-propylene copo-
lymer, respectively. Thus, the examination of the glow curve allowed us to
conclude that the polyblend in question is a heterogeneous one and also re-
vealed the fact that interfacial interaction is rather small. The compari-
son of glow curve of resulting blend and those of initial components allows
to determine its weight ratio with high accuracy.
During the last years the RTL method has been widely used for investigation
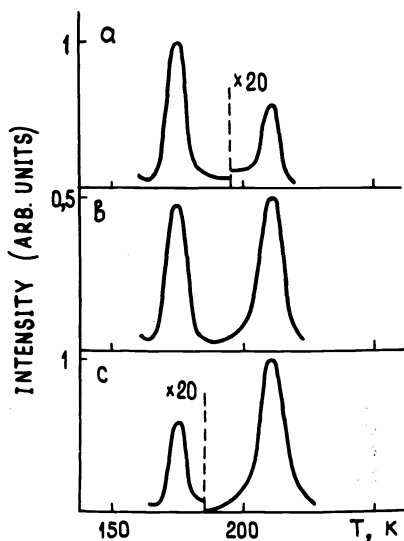

Fig.10. Glow curves for cis-polybutadiene/ethylene-propylene
        copolymer blend. Cis-polybutadiene weight content:
        0,97 (a); 0,50(b); 0,03(c).

of various polyblends and filled polymers as well (41-47). For instance,
interesting results were obtained by Böhm (43) and Kuleznev et al. (44),
who investigated the influence of heat treatment on the structure of cis-
polybutadiene/styrenebutadiene copolymer blend. This blend is known to be
a heterogeneous one, although its glass-transition temperatures are some-
what drawn together, most likely due to the partial solubility of its com-
ponents. It has been established (44), that heat treatment of this blend
at 400-450 K is accompanied by its gradual homogenization, that can finally
result in formation of a single-phase system. Moreover, it appears that
formed this way single-phase structure could be fixed by means of rapid
quenching in liquid nitrogen. The glow curve of the blend, heat treated at
425 K during 40 min. and then rapidly cooled to 77 K possesses one RTL
maximum, located between glass-transition points of initial components.
According to (44), the quenched blend, being heated up to 293 K transforms
once again into a heterogeneous state.
Shershnev and Pestov (45) by means of heating blends of cis-polybutadiene
and styrene-butadiene copolymer of several weight ratios at various tempe-
ratures followed by RTL examination, succeeded in obtaining the phase diag-
ram for this system, shown in Fig. 11. All points located in this diagram
above the curve correspond to formation of a single-phase blend.
The critical composition, as well as the upper critical solution temperatu-
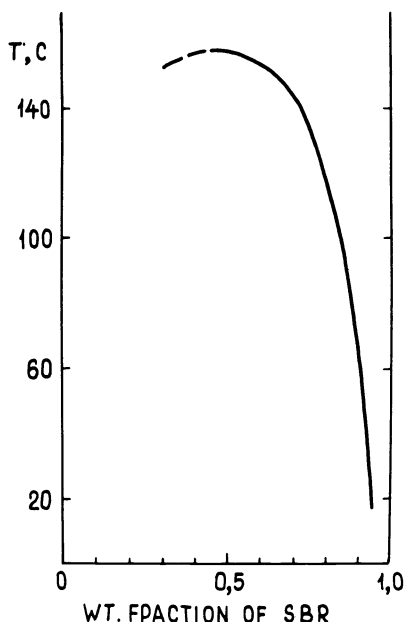re were found to be equal to 37 wt % and 423 K, respectively.

Fig. 11. Phase diagram for PP/BSC blend as revealed from RTL
       data.

It has to be noted that the preparation of a single-phase polyblend by
means of heat treatment of the initially heterogeneous one, followed by its
quenching, is a very complicated task. The majority of polymer-polymer
pairs exhibits either too high upper critical solution temperature or un-
dergo quick phase separation when cooled. The example considered above,
illustrating the preparation of a single-phase blend of polybutadiene and
styrene-butadiene copolymer, is, therefore, an exclusive one.
In conclusion, we consider the results of our study (46, 47) in which an
attempt to prepare polyolefin polyblends with a homogeneous amorphous phase
was made. With that task in view we placed the initial heterogeneous poly-
blends of various polyolefins into a press where they were subjected to
the action of large deformations at 293 K.
The materials tested in this work were isotactic polypropylene (PP)/low
density polyethylene (LDPE) blend, PP/ polyisolutylene blend, PP/ethylene-
propylene rubber (EP) blend and also some others. All these binary polyb-
lends were prepared by successive mutual milling of components in a rotary
crushing mill, subsequent mixing in a Banbury mill at 473 K during 15 minu-
tes with granulation following finally. These granules were then compres-
sion-moulded at 493 K into films 100 µm thick, which were deformed by
shearing, using the installation of Bridgman anvil type. For this purpose
the films were cut into discs with a diameter of about 20 mm, these discs
were placed between anvils (Fig.12) and the anvils were pressed together.
Then we began to rotate the upper anvil about the axis, passing through
its centre, the rotation process occurring under pressures from 0.5 to
20 Kbar and rotation angles varying from 5 to 2000°. Due to this, within
the films arise plastic shearings, their values being proportional to the
product of rotation angle and the average distance between the examined
region of a film and the anvil centre. Preparation and subsequent deforma-
tion of homopolymer films were fulfilled according to the same procedure.
After deformation the discs were removed from the anvil and the central
region with a diameter of about 10 mm was cut out. The structure of the
residual outlying area of a sample was carefully examined. It has to be
noted that the film deformation yielded only in a slight decrease of the
film thickness, the samples being perfectly intact and transparent in most
cases.
The amorphous phase homogeneity of both the initial undeformed films and
films deformed in a press was examined by RTL method and by differential
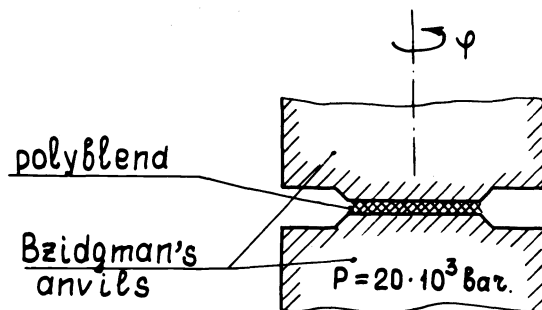scanning calorimetry as well. The application of other structural methods

Fig. 12. The apparatus scheme for the deformation of
         polyblends in a press.

for this purpose appears to be inconvenient, due to the rather small
weight of samples, about 1-3 mg.
In the glow curves of undeformed samples intensive RTL maxima could be ob-
served, located in glass-transition regions. The glass-transition tempera-
tures of EP, polyisobutylene, LDPE and PP samples prepared by slow cooling
of melt to room temperature as determined from the positions of these
maxima, were 212, 218, 225 and 258 K, respectively.
The deformation of LDPE and PP films results in increasing of glass-transi-
tion temperatures, whereas the intensity of RTL maxima decreases. Thus, the
glass-transition temperatures of PP samples, deformed under a pressure of
10 Kbar and a rotation angle of 200 degrees, exceeded that of the initial
film by 8-10 K.
The glow curve of all examined blends, not subjected to shear deformation
in press, represented the sum of the glow curves of its initial components.
(See, for example, the glow curves of PP/EP blend, shown in Fig. 13). This
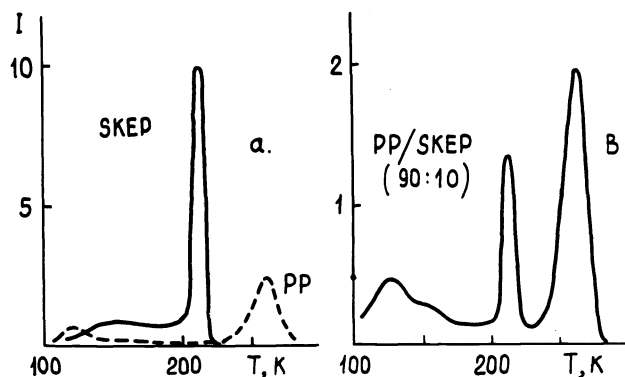

Fig. 13. Glow curves: a - PP and ethylene-propylene rubber
         (EP); b - initial (undeformed) PP/EP blend (weight
         ratio 90 : 10).

result allows us to conclude that the mixing in molten state fails to
achieve compatibility of the PP amorphous phase with EP rubber.
The deformation of PP/EP, PP/LDPE and also some other polyblends in the
press resulted in substantial changes in their structure. It could be con-
sidered on the example of PP/EP polyblend (90 : 10 w/w), deformed under
pressures of 8 Kbar (Fig.14). At the first stage of the deformation process,
when the anvil rotation angle does not exceed 500 degrees, one could obser-
ve some noticeable increase in T_g's value of PP phase; increasing in T_g's
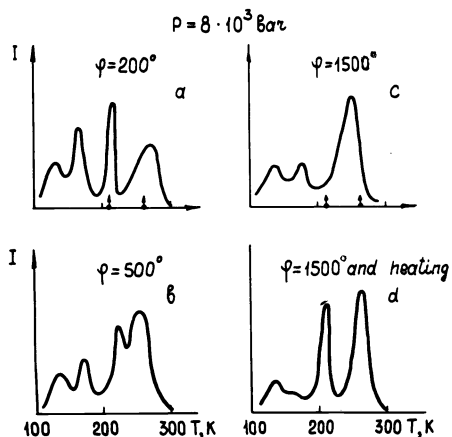value of rubber phase was observed also but to a far smaller extent.

Fig. 14 Glow curves for PP/EP blend (weight ratio 90:10) deformed under pressure of 8 Kbar and anvil rotation angles: a - 200°; b - 500°; c - 1500°; d - the latter sample after heat treatment at 500 K. Arrows in abscissa axis indicate T_g's values of PP and EP components.

Together with that in a glow curve of the deformed blend a maximum, located at 160 K, appeared. For the blend deformed under pressure intervals of 1-5 Kbar this maximum revealed the largest intensity. The intensity of a maximum located at 160 K weakened as the pressure values reached 10-20 Kbar. The main reason of its appearance is most likely the formation of micro-cracks in a deformed film and associated with this process the increase in local molecular relaxation processes.
As the anvil rotation angle exceeded 600-800 degrees, the glass-transition temperatures started gradually draw together. At a rotation angle value of 1500 degrees one could observe a single maximum located at 235-240 K, i.e. the mixture became homogeneous, showing now a single glass-transition tem-perature. The fact that the amorphous phase was a homogeneous one, was supported by means of the DSC method. The degree of crystallinity of a deformed film was found to be 10-20% lower than that of the initial one. For the PP/EP blends deformed under pressures lower than 3 - 5 Kbar, the changes in the initial RTL glow curve were considerably smaller, the com-plete merging of glass-transition maxima not occurring even for the rota-tion angles equal to 2000 degrees.
These polyblends with a single homogeneous amorphous phase are, of course, not in an equilibrium state. Nevertheless, the latter was found to be a rather stable one: for instance, the storage of this homogeneous polyblend at 293 K during a prolonged period of time, as well as its heating up to 380 K were not accompanied by any appreciable changes in the glow curve shape. The main reason hindering the phase separation occurence, is probably the existance of PP crystallites in the examined polyblend. Indeed, the PP/EP homogeneous blend, prepared by deformation under pressures of 5-10 Kbar, did transform into a two-phase heterogeneous state, being heated up to temperatures, exceeding that of PP melting point. The glow curve of a film sample, deformed under a pressure of 8 Kbar and then heated at 500 K (Fig.14d), shows the maxima, located in glass-trasition temperature region of PP and EP, respectively, as is the case for the initial mixtu-re. The structure of homogeneous PP/EP polyblends, prepared under 20 Kbar pressures was found to be more stable to heat treatment: after heat treat-ment at 500 K the blend was still a homogeneous one. The homogeneous PP/LDPE and PP/Butyl-rubber polyblends, as well as several others were prepared according to the same procedure.
Of course, the present paper does not permit to review all the aspects of RTL application to various polymer systems. It is necessary to mention also that this method is successfully applied to study forced high-elasticity of polymers, filled polymers, supermolecular structure of crystallized polymer and also to some chemical processes, accompanied by formation or destruc-tion of macromolecular functional groups, that possess luminescent pro-perties.

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

1. V.G.Nikol'skii and N.Ya.Buben, Dokl. Akad. Nauk SSSR, 134, 134-136 (1960).
2. V.G.Nikol'skii, I.I.Chkheidze and N. Ya.Buben, Kinet. Katal. 5, 82-89 (1964).
3. M.V.Alfimov, V.G.Nikol'skii and N.Ya.Buben, Kinet. Katal. 5, 268-276 (1964).

4. N.Ya.Buben, V.I.Goldanskii, L.Yu.Zlatkevich, V.G.Nikol'skii and V.G.Raevskii, Dokl. Akad. Nauk SSSR, 162, 370-372 (1965); Vysokomol. Soedin. Ser. A , 9, 2275-2283 (1967).

5. V.G.Nikol'skii, Dokl. Akad. Nauk SSSR, 176, 132-134 (1967).

6. V.G.Nikol'skii, Khim. Vys.Energ., 2, 271-273 (1968).

7. V.A.Tochin and V.G.Nikol'skii, Khim. Vys. Energ., 3, 281-282 (1969).

8. V.G.Nikol'skii and G.I.Burkov, Khim. Vys. Energ., 5, 416-421 (1971).

9. V.A.Aulov and N.F.Bakeev, Vysokomol. Soedin., Ser.A , 20, 2338-2343 (1978).

10. S.G.Kiriushkin and Iu.A.Shliapnikov, Dokl. Akad. Nauk SSSR, 232, 845-847 (1977).

11. K.K.Ametov and B.S.Yakovlev, Khim. Vys. Energ., 12, 471-472 (1978).

12. A.Charlesby and R.H.Partridge, Proc. Roy. Soc. Lond., Ser.A, 271, 170-206 (1963); ibid. 283, 329-349 (1965); J.Polym.Sci.,B 1,439-442(1963).

13. I.Boustead and A.Charlesby, Europ. Polym. J.,3, 459-471 (1967); Proc. Roy. Soc. Lond., Ser.A, 316, 291-302 (1970).

14. I.Boustead, Proc. Roy. Soc. Lond., Ser.A, 318, 459-471 (1970).

15. A.Charlesby and G.P.Owen, Int. J. Radiat. Phys. Chem., 8, 343-347 (1976).

16. A.Deroulede, F.Kieffer and M.Magat, Israel. J. Chem., 1, 509-515 (1963).

17. F.Kieffer and M.Magat, in Actions Chimiques Biologiques des Radiations 14 Ser. (Coll. M.Haissinskii) 135-152, Masson, Paris (1970).

18. M.Magat, J.Chim. Phys., 63, 142-149 (1966).

19. W.Knappe, H.-U. Schenker and A.Zyball, Kolloid - Z., Z. Polym., 250, 1135-1138 (1970).

20. J.H.Rancar and R.J.Fleming, J. Polym. Sci, A-2, 10, 1979-1997 (1972).

21. R.J.Fleming, J. Polym. Sci. A-2, 6, 1283-1286 (1968).

22. R.J.Fleming, J. Polym. Sci., Polym. Phys. Ed., 16 , 1703-1704 (1978).

23. S.Radhakrishna and M.Rama Krishna Murthy, J. Polym. Sci, Polym. Phys. Ed., 15, 987-993, 1261-1266 (1977).

24. R.H.Partridge, in Radiation Chemistry of Macromolecules, (M.Dole, ed.) v.1, 193-222, Academic, N.-Y. (1972).

25. V.A.Vonsyatskii and G.Ya.Boyarskii, in New Methods of Polymers Investigation (Yu.S.Lipatov, ed.), 169-191, Nauckova Dumka (1975).

26. V.A.Aulov and N.F.Bakeev, Dokl. Akad. Nauk SSSR, 255, 1400-1403 (1980).

27. Ya.A.Abeliov, V.G.Nikol'skii, V.N.Kirillov and B.F.Alekseev, Vysokomol. Soedin., Ser.A, 20, 2304-2311 (1978).

28. V.G.Nikol'skii, R.A.Terteryan, S.D.Livshiz, N.A.Mironov and T.A.Frolova, Vysokomol. Soedin., Ser.B, 17, 514-518 (1975).

29. R.F.Boyer, Polymer, 17, 996-1008 (1976).

30. L.V.Masagutova, L.Yu.Zlatkevich, V.I.Guseva and V.G.Nikol'skii, Vysoko-mol. Soedin., Ser B, 13, 881-883 (1971).

31. I.Kolthoff, T.S.Lee and C.W.Carr, J. Polym. Sci., 1 , 429-433 (1946).

32. V.G.Nikol'skii, E.P.Danilov, N.A.Mironov and V.L.Karpov, Vysokomol. Soedin., Ser.A, 12, 1288-1293(1970).

33. V.G.Nikol'skii, I.A.Krasotkina, N.S.Tichomirova and I.A.Tubasova, Khim. Vys. Energ., 5, 149-152 (1971).

34. L.E.Nielsen, Mechanical Properties of Polymer and Composites v.1, N.-Y. (1974).

35. V.Nikolskiy, Soviet Sci.Rev., 3 , 77-82 (1972).

36. V.N.Dinzburg, N.V.Smirnova, V.N.Alekseenko and V.G.Nikol'skii, Kauch. Resina N 12,5-7 (1970).

37. V.G.Nikol'skii, L.Yu.Zlatkevich, V.A.Borisov and M.Ya.Kaplunov, J. Polym. Phys. Ed. 12, 1259-1265 (1974).

38. P.Corish, Rubber Chem. Technol., 40, 324-340 (1967).

39. P.A.Marsh, A.Voet and L.D.Price, Rubber Chem. Technol. 40, 359-367 (1967); ibid., 41, 344-355 (1968).

40. L.Yu.Zlatkevich and V.G.Nikol'skii, Rubber Chem. Technol. 46, 1210-1217 (1973).

41. Yu.S.Lipatov, V.A.Vonsyatskii, E.P.Mamunya and G.Ya.Boyarskii, Vysokomol. Soedin., Ser B, 16, 838-839 (1974).

42. O.L.Mel'nikova, V.N.Kuleznev, V.A.Aulov and V.D.Klykova, Vysokomol. Soedin., Ser.B, 18, 903-906 (1976).

43. G.G.Bohm, K.R.Lucas and W.G.Mayer, Rubber Chem. Technol. 50, 714-722 (1977).

44. S.S.Pestov, V.N.Kuleznev and V.A.Shershnev, Kolloidn. Zh. 40, 705-711 (1978).

45. V.A.Shershnev and S.S.Pestov, Kauch. Resina N 9, 11-19 (1979).

46. V.A.Zhorin, N.A.Mironov, V.G.Nikol'skii and N.S.Enikolopyan, Dokl. Akad. Nauk SSSR,244, 1153-1156 (1979).

47. V.A.Zhorin, N.A.Mironov, V.G.Nikol'skii and N. S.Enikolopyan, Vysoko-molec. Soedin., Ser.A, 22, 397-403 (1980).