Properties and Phase Structure of the Poly(propylene)-Low-Density Poly(ethylene) Blends

N. M. Livanova[a]; E. S. Popova[a]; O. A. Ledneva[a]; A. A. Popov[a]

[a] Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

PLEASE SCROLL DOWN FOR ARTICLE

Properties and Phase Structure of the Poly(propylene)-Low-Density Poly(ethylene) Blends

N. M. LIVANOVA*, E. S. POPOVA, O. A. LEDNEVA and A. A. POPOV

Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 117977 Russia

The phase structures of PP-LDPE blends in isotropic and oriented states were studied by the methods of DSC and polarization IR spectroscopy. The composition intervals were established that correspond to the formation of interpenetrating network structures. The presence of LDPE increases the degree of PP orientation and the mechanical strength of the blends. This indicates that LDPE acts as a structure-modifying agent, while PP plays the role of strengthening (reinforcing) filler. A relationship between the deformation and strength properties of the oriented films of the PP-LDPE blend and the phase structure of the PP component is demonstrated. The stability of the blend to oxidation in the ozone-oxygen medium is determined by the structure of a less stable system component (PP). The oxidation rate reaches maximum in samples with an isotropic PP structure and is minimum in the blends with highly oriented PP component.

Keywords: Phase structure; polypropylene-polyethylene blends; mechanical properties; deformation; oxidation; structure analysis

INTRODUCTION

The creation of new materials by blending polymers possessing high mechanical properties and stability to aggressive media (primarily oxygen and ozone) implies controlled modification of the component structures. Despite numerous publications on the subject, there are

---

*Corresponding author.

many questions that still remain unclear. The polymer blends are frequently studied by measuring integrated characteristics which are difficult to relate to the phase structure of a particular polymer component or a transition layer in the system.

The properties of polyolefin blends, like those of other polymers, are nonlinear functions of the blend composition [1–3]. The most extensively studied system comprises the PP-HDPE blends which are characterized (at proper compositions) by high values of the tensile strength, modulus, and impact strength, and low embrittlement temperatures. The supermolecular structures, structural and dynamic parameters of amorphous regions, mechanical properties, and oxidation behavior of these systems with various molecular-mass characteristics of the components were described in [4–10]. The PP-LDPE blends were studied to a lower extent, although these systems are of interest from both fundamental and applied standpoints. Nielsen [1] pointed out the possibility to control the degree of orientation in these blends and their applicability to the film production.

The purpose of this work was to study the structures of components in the PP-LDPE blends having various compositions by the methods of polarization IR spectroscopy and DSC. The former method provided data on both the supermolecular structure and the fine molecular structure of amorphous regions in both polymer phases of the blend.

EXPERIMENTAL

Experiments were performed on isotropic and oriented films prepared from blends of isotactic PP ($M_w = 4 \times 10^5$; $M_n = 1.5 \times 10^5$; $M_w/M_n = 2.7$) and LDPE ($M_w = 3.6 \times 10^4$; $M_n = 1.2 \times 10^4$; $M_w/M_n = 3$) having about 25 branching junctions per 1000 carbon atoms (estimated by the formula $N = 13.0\ D_{1377}$, where N is the number of methyl groups per 1000 carbon atoms, and D_{1377} is the optical density of the absorption band at 1377 cm^{-1} measured at room temperature in a 1 mm thick film [11]).

The blends were prepared as described elsewhere [12]. The isotropic films were obtained by molding at 463 K and a pressure of 1.5×10^7 Pa on a cellophane substrate, followed by quenching in water at 273 K. The orientational drawing of the films was performed by local heating

at 353 K (PP/LDPE ratio varied from 0:100 to 65:35) and 383 K (PP/LDPE = 80:20 – 100:0). The drawing ratio $\lambda = L/L_0$ fell within the range of 3 – 5.5, which is optimum for the given blend composition and orientation conditions. The films were also characterized by the maximum degree of drawing at 383 K (Fig. 1). The film thickness was approximately 20 μm.

The degree of crystallinity κ and the melting temperatures T_m of crystallites of each component in the blend in the isotropic and oriented state were determined by DSC measurements [13] performed on an SKM-2M calorimeter operated at a temperature scan rate of 8 K/min. The average melting temperatures were determined at the maximum of the melting peaks on the DSC thermograms.

The deformation and strength properties were studied by the method of stepwise loading [14] on oriented samples. The tests were performed in vacuum at 383 K on a setup for durability testing with the deformation recorded [15].

The structures of the blend components were studied by polarization IR spectroscopy on an UR-20 spectrophotometer.

The degree of orientation of the PP component was characterized by dichroism of the bands of regular conformers $R = D_{\parallel}/D_{\perp}$, determined for the bands of parallel polarization at 840 and 998 cm^{-1}, and the I/R ratio for the perpendicularly-polarized band at 810 cm^{-1}, where $D_{\parallel}$ and $D_{\perp}$ are the optical density of the band measured in the
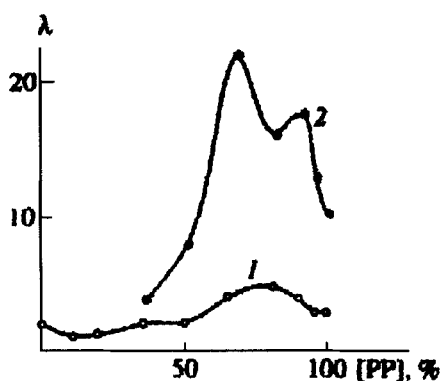

FIGURE 1 The plots of (7) optimum and (2) limiting drawing ratios of PP-LDPE blends *versus* the PP content.

light of parallel and perpendicular polarization, respectively [16, 17]. The degree of LDPE orientation was determined from dichroism of the bands of perpendicular orientation at 720 and $730\,\mathrm{cm}^{-1}$ (1/R).

The contents of various LDPE conformations were calculated as the ratio of the optical density at the maximum of the corresponding band to the optical density of a structure-insensitive band at $1470\,\mathrm{cm}^{-1}$ [18] normalized to the fraction of LDPE in the blend $(1-a)$, where a is the fraction of PP in the blend. Note that the absorption intensity at $1470\,\mathrm{cm}^{-1}$ contains contributions from both components of the PP-LDPE blend having close values of the absorption coefficient K. The band at $1460\,\mathrm{cm}^{-1}$ in the IR spectrum of PP belongs to the asymmetric bending vibrations of CH_3, and the band at $1470\,\mathrm{cnr}^{1}$ in the spectrum of PE is due to the bending vibrations of CH_2 [11, 19]. The internal standard for PP can be represented by the band at $1168\,\mathrm{cm}^{-1}$, while most of the bands in the spectrum of LDPE are masked by intensive absorption of PP. In order to check the correctness of using the band at $1470\,\mathrm{cm}^{-1}$ for determining the relative band intensities of both polymer components, we have studied the ratio of the optical intensities of the bands at 1170 and $1470\,\mathrm{cm}^{-1}$ divided by the proportion of PP in the blend (Fig. 2). This ratio was weakly dependent on the blend composition, which was evidence of the close values of the partial absorption coefficients of the two components at a frequency of $1470\,\mathrm{cm}^{-1}$. The corresponding correction factor was introduced in calculating the relative optical densities of LDPE bands; the relative error of the determination was about 15%.

An analysis of the conformation composition of the segments of LDPE macromolecules in the intercrystallite regions was possible only
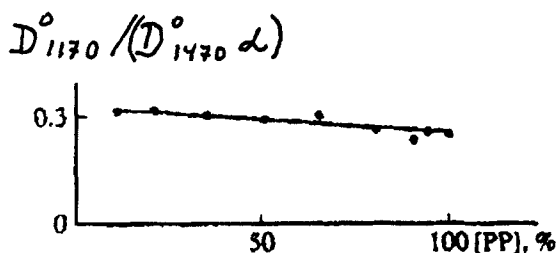

FIGURE 2   Effect of composition on the ratio of optical densities of the bands at 1170 and $1470\,\mathrm{cm}^{-1}$ in the IR spectra of PP-LDPE blends.

on the basis of two sufficiently intense bands observed at 720 and
730 cm^{-1} [16, 20]. The band at 730 cm^{-1} (σ, the angle of the transi-
tion momentum, 83°) corresponds to crystallites [20] and has the inten-
sity depending on the content of chain segments in the flat zigzag
conformation with a segment length of m > 7. The band at 720 cm^{-1}
reflects the content of shorter sequences in the trans conformation
($7 \geq m \geq 2$) in both the amorphous and crystalline regions [21]. The
total amount of gauche isomers in the intercrystallite regions of LDPE
was calculated by the formula

$$G = T_c/\kappa - (T_c + T_a),\eqno(1)$$

derived from the equation [16]

$$\kappa = (I - p)/(I + 1),$$

where κ is the degree of crystallinity determined by DSC, $I = (T_c + T$
$T_a)/G$, $p = T_a/G$, T_c and T_a are the content of trans isomers in the
crystalline and amorphous regions, respectively, and G is the content
of gauche isomers.

The total content of trans isomers in the crystalline and amorphous
regions ($T_c + T_a$) was determined from the intensity of the absorption
band at 720 cm^{-1}, and the T_c values were determined using the band
at 730 cm^{-1}. The optical densities were related to the fraction of
optical density of the band of the internal standard at 1470 cm^{-1}
assigned to LDPE. Because the extinction coefficients of the bands at
720 and 730 cm^{-1} are different [21] ($K_{730}/K_{720} = 1.67$), the intensity of
the band at 720 cm^{-1} used in calculations of the amount of trans
isomer was multiplied by the corresponding factor (1.67):

$$D_G = D^\circ_{730}/[D^\circ_{1470}(1 - a)\kappa] - D^\circ_{720} \, 1,67/D^\circ_{1470}(I - a).$$

RESULTS AND DISCUSSION

The isotactic PP and LDPE are thermodynamically incompatible
polymers forming crystalline lattices of different types [22, 23]. Because

of the different melting temperatures of the two polymers, their structures in the blend are separately formed under different conditions [24]. At a higher solidification temperature of the minor component, the structure formation in this component is hindered, and the process in the matrix depends on the component panicle distribution. At a lower solidification temperature of the minor component, the structure formation in the major component proceeds more perfectly.

Upon the phase inversion and the formation of a continuous spatial network of the second component, deformation of the samples will be accompanied by orientational rearrangement in the structure.

Figure 3 shows the plots of the degree of crystallinity and the melting temperatures of PP and LDPE crystallites in the isotropic and oriented blends. The regions of small content of the second component exhibit extrema. As the PP content increases, the degree of crystallinity of the LDPE component in the isotropic samples decreases, while the degree of crystal perfection (characterized by the T_m value) somewhat increases. The degree of crystallinity of the PP component varies according to a complicated law, while the T_m value of these crystallites remains the same for all compositions (except the compositions with PP/LDPE = 20:80 and 35:65, where the crystal perfection exhibits a sharp drop).
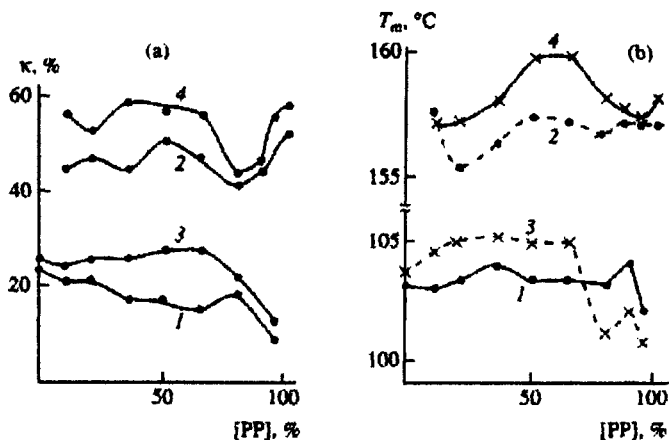

FIGURE 3   Effects of PP-LDPE blend composition on (a) the degree of crystallinity and (b) crystallite melting temperature: (1,3) LDPE; (2,4) PP; (1,2) isotropic; (3,4) oriented.

The degree of crystallinity and the crystal perfection of both components increases as a result of the orientational drawing. An exception is observed for the blends with LDPE contents below 35%, where both characteristics exhibit a sharp drop. This behavior can be explained by the effects of drawing conditions of the structures of component polymer phases. Upon drawing at 353 K, which is significantly below the melting point of LDPE, the samples exhibit a higher degree of crystallinity and higher T_m values of the crystals as compared to those in the isotropic blends. The drawing at 383 K, that is, above the melting temperature of LDPE (376 K), seems to result in a partial melting of the LDPE crystallites in the subsurface layer of the sample. The metastable state of these partly melted crystallites is frozen when a sample rapidly leaves the heating zone.

The lower values of κ and T_m of LDPE in the isotropic mixtures with PP/LDPE = 95:5 compared to those for individual LDPE imply a strong amorphization of the PE particles. Apparently, a certain amount of LDPE is dissolved in the PP phase. As the LDPE content in the blend increases above 5%, the blends feature a phase separation leading first to an increase in the LDPE concentration (90:10 blend) followed by a growth in the particle size (80:20 blend) and the formation of a well developed transition region between the two polymer phases. The latter compositions have the minimum values of the degree of PP crystallinity, because the presence of a large number of the LDPE inclusions hinders the formation of a highly crystalline PP structure. As the LDPE content in the blend increases further, the LDPE particles merge together, and interphase boundary surface decreases (65:35 blend).

The orientational drawing at 383 K increases the proportion of the amorphous LDPE phase. This is caused by breakage of the small LDPE crystallites (formed upon cooling) under the action of the drawing temperature and shear stresses. However, the continuity of the polymer matrix is not perturbed and the adhesive bonds between the disperse phase and the dispersion medium are retained. This is evidence of a strong contact between the two polymer phases and the presence of a sufficiently strong transition layer. Besides the seg-mental solubility, an increase in the strength of the transition layer is favored by the formation of mechanical entanglements of the dissimilar polymer molecules upon the high-temperature mechanical mixing taking place in the extruder and in the mold.

The results of investigation of the oriented blend system with the aid of the polarization IR spectroscopy confirms the above pattern and adds a number of significant details and refinements.

Figure 4a presents data on the degree of orientation of the PP phase, as determined from the dichroism of various absorption bands of the regular PP conformations. Figure 4b shows the corresponding data for LDPE. Using the dependence of dichroism of the absorption bands on the blend composition, we may readily determine the interval of component compositions corresponding to the phase inversion and the interpenetrating network structure formation. The growth in the degree of orientation in the crystalline PP regions begins at a PP content of 35%. Therefore, this (and higher) PP concentration in the isotropic samples corresponds to the formation of a condensation (cross-linked) structure in which the extent of fibrillization increases with the PP content. By the same token, the growth of dichroism of the absorption bands of the regular LDPE conformations (Fig. 4b) is observed for the LDPE content in the blend above 20%. A jump in the degree of orientation of the crystalline LDPE regions (measured by the intensity of the band at $730\,cm^{-1}$) in the 35 : 65 blend is probably explained by facilitated orientational rearrangement in the isotropic films as a result of the formation of a spatial PP network, which is also involved in the deformation process. A reduction in the degree of LDPE orientation upon further decrease in its concentration can be explained
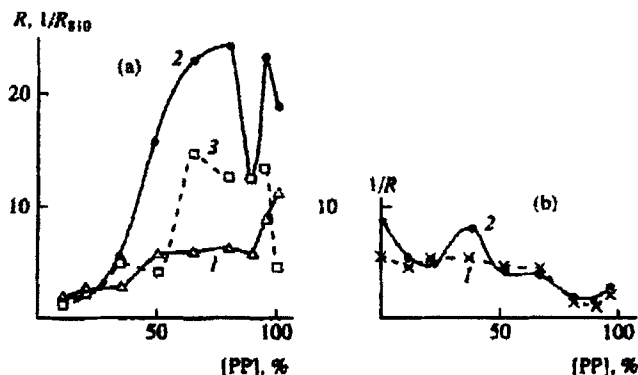

FIGURE 4   Effect of the PP-LDPE blend composition on the dichroism of the (a) PP and (b) LDPE bands in the IR spectra (cm^{-1}): (1a) 810; (2a) 840; (3a) 998; (1b) 720; and (2b) 730.

by a more independent participation of both components in the fibrillization process. As noted above, the samples with small LDPE contents (5 – 10%) feature amorphization of the LDPE particles. This is confirmed by the results of calculation of the number of gauche isomers and the ratio of trans to gauche isomers in the amorphous LDPE regions using formulas (1) and (2) (Fig. 5). Indeed, an increase in the degree of LDPE dispersion is accompanied by a sharp increase in the proportion of the folded gauche conformation at the expense of a decrease in the content of regular trans isomers. At a 20% LDPE content, the size of the crystalline particles apparently increases, and their degree of crystallinity approaches that of the individual polymer, which results in a sharp growth in the trans to gauche isomer ratio.

Data on the true degree of orientation in the regular PP conformation (Fig. 4a) indicate that orientation of the PP component in the blend is higher than that in the individual polymer (except the data for the absorption band at $810 \, \text{cm}^{-1}$, for which the dichroic ratio is lower in the blend than in the polymer). Therefore, the LDPE component in the blend with PP acts as a structure-modifying agent facilitating the formation of isotropic films, favoring structural rearrangements, and increasing the degree of orientation of the PP component. This is manifested by an increase in the limiting drawing ratio λ_{lim} of the oriented blends (Fig. 1, curve 2). Since the drawing
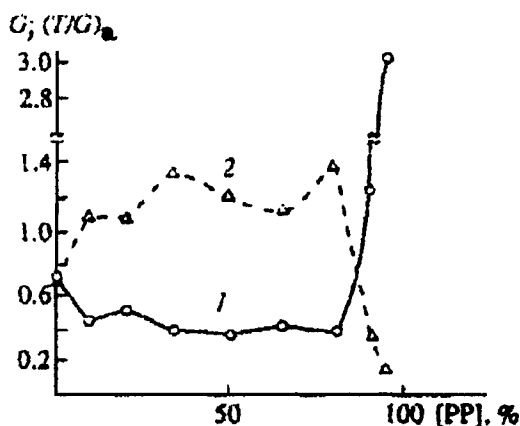

FIGURE 5   Effect of the PP-LDPE blend composition on (1) the content of gauche isomers G and (2) the trans to gauche isomer ratio T/G in the amorphous LDPE regions.

temperature (383 K) was higher than the melting temperature of LDPE crystallites (Fig. 3b), the LDPE component apparently occurs in the state of pre-melting (that is, in a strongly amorphized form) in all samples irrespective of the structure existing in the initial films. Dependence of the λ_{lim} value on the composition characterizes deformability of the PP framework and is correlated with variation in the degree of orientation of the crystallites and the shortest tie chains of PP (see data for the bands at 840 and 998 cm^{-1} in Fig. 4a).

A similar dependence was obtained for the limiting stress leading to irreversible plastic deformations of the PP framework (that is, for the creep stress (σ_{cr}) presented in Fig. 6). The higher the degree of PP orientation and the system rigidity, the greater the σ_{cr} values. The maximum of σ_{cr} observed for the 95:5 composition is indicative of a hindered plastic deformation (increased rigidity) in the samples during the phase separation, that is, in the presence of the second component whose macromolecular chains are probably strongly bound to the amorphous PP component by mechanical entanglements. In this blend composition, LDPE partly occurs in the dissolved state, while the content of LDPE in the transition (intercrystallite) PP regions is relatively small. Thus, data on the deformation-strength characteristics (σ_{cr} and λ_{lim}) can be used in the analysis of the structure of fibrillized polymer blends. A continuous framework formed by PP microfibrils plays the role of a reinforcing filler, markedly increasing the mechanical properties of the material.
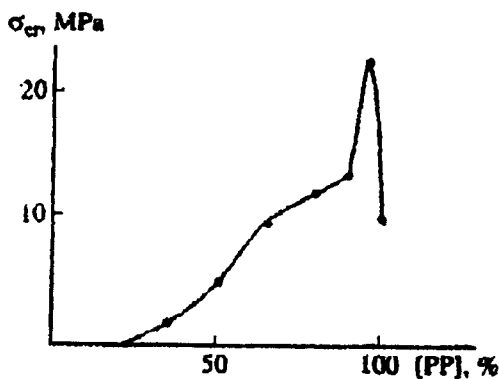

FIGURE 6   Effect of the PP-LDPE blend composition on the limiting creep stress σ_{cr}.

Data reported in [4–10] showed that the oxidation by ozone is a promising model reaction for the investigation of structure formation in the blends of various polymers, including polyolefins. Figure 7 shows a dependence of the oxidation rate of the PP-LDPE blend on the sample composition. The oxidation was performed in an ozone-oxygen mixture containing $0.5 \, mol/m^3$ ozone. The samples were exposed to this mixture for 2 h at room temperature in the unloaded state (curve 1) and under a 60 MPa load (curve 2).

A comparison of data on the rate of ozone-induced oxidation in the oriented films (Fig. 7) and the degree of orientation of the PP and LDPE components (Fig. 4a) shows that these quantities vary in opposite directions. Therefore, chemical stability of the blend (in particular, toward the ozone action) is determined to a considerable extent by the supermolecular and molecular structures of the amorphous regions of the less stable polymer component of the blend. In the oriented state, the oxidation rate of LDPE is 1/2 of that for PP, despite the fact that the former polymer exhibits a markedly lower ability to orientation and the degree of orientation. This is explained by a high reactivity of the tertiary carbon atom compared to that of the secondary carbon. In the isotropic state of PP (10:90–35:65
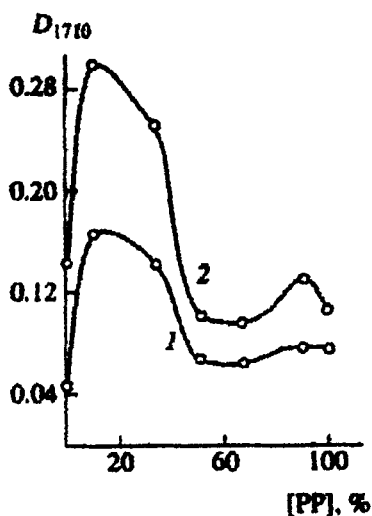

FIGURE 7 Effect of the PP-LDPE blend composition on the product accumulation rate during oxidation in an ozone-oxygen medium at $\sigma = 0$ (1) and 60 MPa (2).

blends), taking into account a high rate of the PP oxidation, the ob-
served features of the oxidation kinetics depend not only on the phase
structure of the PP component, but on the matrix structure, the size of
dispersed PP particles, and the volume and structure of the transition
layer as well.

It was demonstrated that the stability of polyolefins with respect to
thermal oxidation and the ozone action increases with the drawing
ratio and varies in phase with decreasing segmental mobility (as
determined by the correlation time of a radical probe) [25]. The effect
was attributed to an increase in the number of steric obstacles, the
density of amorphous phase, and confor-mational constraints, and to
a decrease in the segmental mobility, mutual solubility, and micro-
diffusion constants. It is therefore naturally assumed that the same
mechanisms retarding the oxidation process are operative in the ori-
ented polymer blends. Thus, a decrease in the rate of ozone-induced
oxidation in the oriented blends with increasing PP content can be
explained by structural stabilization of the readily oxidized blend com-
ponent as a result of the growing orientation.

An increase in the rate of oxidation in the ozone-oxygen medium
upon loading (Fig. 7, curve 2) can be explained, on the one hand, by
enhanced ozone interaction with the stressed fragments of polymer
macromolecules (this is related with facilitated transhybridization of
the tertiary carbon atom from sp^3 to sp^2 state upon detachment of an
H atom [25]) and, on the other hand, by the role of mechanical ini-
tiation. The maximum growth of the reaction rate is observed in the
systems where PP is present in the form of weakly bound isotropically
particles, while the minimum increase in the oxidation rate takes place
in the region of blend compositions corresponding to the formation of
highly oriented PP microfibrils. This can be related to a high content of
overstressed bonds caused by nonuniform stress redistribution in the
former systems, and a small number of the overstressed macromole-
cular fragments in the intercrystallite PP fragments (due to a lower
scatter of the tie chain lengths in the PP microfibrils) in the latter case.

Thus, the blends studied in this work can be divided into groups
with respect to the type of the major polymer component. The blends
based on a "softer" polymer with additions of a rigid-chain com-
ponent can be considered as analogous to the reinforced thermo-
plasts, while compositions based on the "rigid" component with the

flexible-chain additions are similar to the structurally modified thermoplasts. Systems belonging to the region of continuous phases of both components combine the properties of both groups.

References

[1] Nielsen, L. E. (1974). Mechanical Properties of Polymers and Composites, New York: Marcel Dekker.
[2] Polymer Blends, Paul, D. R. and Newman, S. (Eds.) (1978). London: Academic, Vol. 2.
[3] Kuleznev, V. N. (1980). Smesi polimerov (struktura i svoistva) (Polymer Blends: Structure and Properties), Moscow: Khimiya.
[4] Fridman, M. L. and Prut, E. V. (1984). *Usp. Khim.*, **53**(2), 309.
[5] Erina, N. A., Kompaniets, L. V., Prut, E. V. and Enikolopyan, N. S. (1987). *Mekh. Kompozit. Mater.*, No. 6, p. 963.
[6] Popov, A. A., Zaikov, G. E., Prachella, M. and Martushelli, E. (1982). *Vysokomol. Soedin., Ser. A*, **24**(11), 2336.
[7] Popov, A. A., Russak, A. V., Gladilin, M. P. and Zaikov, G. E. (1986). *Vysokomol. Soedin., Ser. A*, **28**(5), 1083.
[8] Popov, A. A., Russak, A. V., Ledneva, O. A. and Zaikov, G. E. (1986). *Vysokomol. Soedin., Ser. A*, **28**(9), 1836.
[9] Blinov, N. N., Popov, A. A., Rakovski, S. K., Stoyanov, A. K., Shopov, D. M. and Zaikov, G. E. (1989). *Vysokomol. Soedin., Ser. A*, **31**(10), 2213.
[10] Karpova, S. G., Popov, A. A., Zaikov, G. E., Barabash, K. and Mesko, M. (1991). *Vysokomol. Soedin., Ser. A*, **33**(12), 2585.
[11] Zbinden, R. (1964). Infrared Spectroscopy of High Polymers, New York: Academic.
[12] Ledneva, O. A., Popov, A. A. and Zaikov, G. E. (1990). *Vysokomol. Soedin., Ser. B*, **32**(10), 785.
[13] Bershtein, V. A. and Egorov, V. M. (1990). Differentsial'naya skaniruyushchaya kalorimetriya v fizikokhimii polimerov (Differential Scanning Calorimetry in the Physical Chemistry of Polymers), Leningrad: Khimiya.
[14] Livanova, N. M. and Zaikov, G. E. (1989). *Vysokomol. Soedin., Ser. B*, **31**(9), 649.
[15] Livanova, N. M., Rapoport, N. Ya., Miller, V. B. and Musaelyan, I. N. (1976). *Vysokomol. Soedin., Ser. A*, **18**(10), 2260.
[16] Dechant, J., Danz, R., Kimmer, W. and Schmolke, R. (1972). In: *Ultrarotspektroskopische Untersuchungen an Polymeren*, Berlin: Akademie.
[17] Schmidt, P. G. (1963). *J. Polym. Sci. A.*, **1**(7), 2317.
[18] Kissin, Yu. V., Tsvetkova, V. I. and Chirkov, N. M. (1965). *Vysokomol. Soedin.*, **7**(7), 1288.
[19] Samuels, R. J. (1981). *Macromol. Chem. Suppl.*, **4**, 241.
[20] Pakhomov, P. M. (1987). Doctoral (*Chem. Sci.*) Dissertation, Moscow State University.
[21] Pakhomov, P. M. (1975). *Vysokomol. Soedin., Ser. A*, **17**(12), 2612.
[22] Geil, P. H. (1968). Polymer Single Crystals, New York: Interscience.
[23] Crystalline Olefin Polymers, Raff, R. A. V. and Doak, K. W. (Eds.) (1967). New York: Interscience.
[24] Fizikokhimiya mnogokomponentnykh polimernykh sistem (Physical Chemistry of Multicomponent Systems), Lipatov, Yu. S. (Ed.) (1986). Kiev: Naukova Dumka.
[25] Popov, A. A., Rapoport, N. Ya. and Zaikov, G. E. (1987). Okislenie orientirovannykh i napryazhennykh polimerov (Oxidation of Oriented and Stressed Polymers), Moscow: Khimiya.