ISSN 0965-545X, Polymer Science, Ser. A, 2006, Vol. 48, No. 6, pp. 627–632. © Pleiades Publishing, Inc., 2006.
Original Russian Text © L.M. Yarysheva, D.A. Panchuk, S.V. Moiseeva, O.V. Lebedeva, A.V. Bol'shakova, A.L. Volynskii, N.F. Bakeev, 2006, published in Vysokomolekulyarnye Soedineniya, Ser. A, 2006, Vol. 48, No. 6, pp. 970–976.

Mechanism of Fracture of Metallic Coating during Uniaxial Stretching of Substrate Polymer at Temperatures below Its Glass Transition Temperature[1]

L. M. Yarysheva[a], D. A. Panchuk[a], S. V. Moiseeva[b], O. V. Lebedeva[c], A. V. Bol'shakova[a], A. L. Volynskii[a], and N. F. Bakeev[a]

[a] *Faculty of Chemistry, Moscow State University,*
Leninskie gory, Moscow, 119992 Russia
[b] *Moscow State Pedagogical University,*
Nesvizhskii per. 3, Moscow, 119882 Russia
[c] *Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,*
ul. Profsoyuznaya 70, Moscow, 117393 Russia
e-mail: Yarysh@mail.ru

Received June 6, 2005;
Revised Manuscript Received December 9, 2005

Abstract—The mechanism of fracture is studied for a thin metallic (platinum, gold) coating deposited onto the surface of glassy poly(ethylene terephthalate) that is subjected to uniaxial stretching. The structure of the surface layer in the deformed polymer and the size distribution of the fragments produced by fracture are analyzed. Fragmentation of the coating is shown to take place in a narrow region between the undeformed polymer and the forming neck. Examination of this region allows one to distinguish two different stages of fracture. At the initial stage, the deposited coating randomly breaks down into fairly large fragments. In the region of main orientational transformation of the polymer (in the zone of the forming neck), the predominant mechanism of fracture in the coating is breaking of large fragments formed at the first stage into two equal parts. This mechanism of fragmentation is shown to be universal and independent of the nature of the metal.

DOI: 10.1134/S0965545X06060113

INTRODUCTION

Deposition of a thin metallic or semiconducting layer onto the surface of polymer films allows preparation of materials with new valuable properties. In particular, such films can be used as packaging materials or flexible mirrors, as well as oxygen-proof, sensory, magnetic, or conducting materials [1–8]. However, when a polymer film with a rigid surface layer is subjected to deformation or thermal treatment, the deposited coating may break down and its monolithic structure may be disrupted. To determine the safe interval of service conditions for such materials, it is necessary to gain clear knowledge concerning the mechanism of fracture in rigid coatings deposited onto polymer substrates and to study the effect of the nature of both polymers and coating materials on this process.

Furthermore, deformation of polymers with a thin rigid coating under certain conditions leads not only to breaking of the surface layer into separate fragments but also to the formation of a regular surface microtopography; as a result, such materials acquire other valuable properties [9–15]. For example, such systems are able to provide definite orientation of molecules in liquid crystals, while imparting novel optical properties to the resultant materials [8, 16].

The common features and distinctions in the surface-layer structure of polymer samples with a thin rigid metallic coating during their stretching at temperatures above and below T_g has been described in our earlier studies [10, 14, 17]. The mechanisms of fragmentation and topography formation in the surface layer of coatings that are deposited onto rubbery polymer substrates subjected to stretching have been described in detail [9, 10, 14]. However, when the polymer substrate is stretched at temperatures below T_g, the coating fragmentation mechanism is known to a lesser extent. The objective of this study is to investigate the fracture mechanism of a thin metallic (platinum or gold) coating during uniaxial stretching of amorphous glassy PET. This study also attempts to answer the question about the existence of fundamental differences between the mechanisms of coating fragmentation on a glassy polymer and fragmentation during deformation of a polymer above T_g (the case studied earlier).

---

[1] This work was supported by the Russian Foundation for Basic Research, project nos. 03-03-32748 and 03-03085.

EXPERIMENTAL

In this study, we investigated commercial films of amorphous unoriented PET with a thickness of 100 μm. The samples were cut in the form of dumbbells with a gauge size of 6 × 20 mm. The surfaces of the polymer films were decorated with thin platinum or gold layers via Eiko IB-3 sputtering equipment. The thickness of the deposited layer was controlled by the deposition time and ranged from 2.7 to 27 nm. Then, the test films were stretched at a strain rate of 0.2 mm/min using an Instron-1122 dynamometer. The structure of the films was studied using a Hitachi S-52 scanning electron microscope and a Nanoscope-111a atomic force microscope (Digital Instruments, Santa Barbara, United States) in the contact scanning mode. The numerical values of the mean dimensions of the fractured coating fragments were estimated from the corresponding SEM and AFM images with the use of the Femtoscan Online software.

RESULTS AND DISCUSSION

In [18, 19], the possible mechanisms responsible for the fracture of a rigid coating on a pliable substrate were theoretically analyzed for rubbery polymers. In the case of uniform deformation of the polymer substrate, fragmentation of the coating at early stages of deformation (at low tensile strains of the polymer substrate) is primarily determined by surface microdefects, which are known to exist in any real solid and to initiate fracture of the coating at their localization sites. Such defects are randomly distributed in the coating; hence, the induced fracture of the coating is also irregular and random. However, this initial stage of random fracture is followed by a highly intriguing and unique process, where each fractured fragment experiences further breakdown.

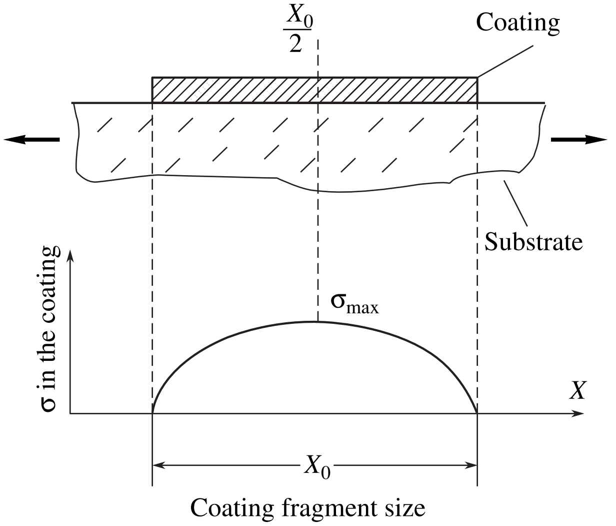

Fig. 1. Schematic representation of stress distribution in a fragment of a coating during tensile drawing of the polymer substrate. X_0 is the size of the fragment. Arrows show the direction of stretching.

The point is that, after this initial stage of random fracture of the coating, the process of substrate stretching still develops and each fractured fragment remains under the action of a tensile stress. The stress distribution in each fractured fragment is highly nonuniform. Evidently, the stress at the ends of each fragment is zero. With increasing distance from the ends, the stress in each fractured fragment increases; precisely at the center of the fragment, it attains the maximum value. Figure 1 shows the schematic representation of stress distribution in the separate fragments of a coating during tensile drawing of the polymer substrate.

As the tensile strain of a rubbery polymer is increased, the stress in the sample also steadily increases. Therefore, the stress in each separate fragment becomes higher and equal to the strength of the coating. This stress level is at first attained precisely at the center of the fragment. As a result, this behavior leads to the fascinating process where the fracture of the coating proceeds via disintegration of each fragment into two equal parts. This mechanism of fracture is active while the soft and compliant substrate is able to transfer a stress exceeding the strength of the coating to fragments of the coating. Once the dimensions of all fragments become so small that the substrate is no more capable of transferring the breaking stress to them, this disintegration process is terminated. For the above reasons, the dimensions of the fragments finally become more or less equal to each other and the resultant size distribution of the fractured fragments formed on the surface of the polymer substrate is very narrow. Hence, one can conclude that fracture of a coating on a rubbery polymer substrate proceeds via both random fracture and disintegration of the fragments into two parts.

As is known, deformation of amorphous polymers below their glass transition temperature is not uniform and transition of the polymer into the oriented state takes place via the formation and growth of either necks or crazes.

Fragmentation of a coating during nonuniform deformation of the polymer substrate (PET) below T_g and, in particular, during its stretching in the presence of adsorption-active liquid media via the classical crazing mechanism was studied in [15]. In this case, polymer deformation is observed within specific local regions referred to as crazes. Crazes are separated by regions of the undeformed polymer, which are gradually transformed into crazes as the latter expands. Fragmentation of the coating takes place within the narrow boundary between a craze and a region of the undeformed bulk polymer. In this case, one can observe the formation of long thin strips of virtually equal widths, which are oriented strictly perpendicular to the direction of tensile drawing and parallel to each other. The mechanism of fragmentation is assumed to consist in detachment of equal-size fragments from edges in the boundary region between a craze and the undeformed polymer.

The mechanism of coating fragmentation during nonuniform polymer deformation (via necking) at temperatures below T_g has not yet been studied from this standpoint. Deformation of a polymer sample via crazing during drawing in adsorption-active media and deformation of a polymer in the air via necking have many common features. In both cases, the character of deformation is highly nonuniform and the resultant structure contains coexisting regions of locally oriented and unoriented polymer. Hence, one can also expect many common features in the mechanisms of coating fragmentation during tensile drawing of polymer substrates according to these two different deformation modes.

However, in addition to many similar features, there are certain differences between fragmentation of the coating in a neck and in crazes [15, 17]. The coating fragments in the neck region have a less uniform size distribution and are located at a certain angle with respect to the axis of tensile drawing of the polymer substrate. Furthermore, Fig. 2 presents an AFM image where fracture (into two parts) of some fragments formed during uniaxial stretching of a glassy PET sample with a platinum coating is seen to begin in their central regions. This observation implies that the possibility of the coating fracture via disintegration into two parts is not excluded even during deformation of a glassy polymer that is accompanied by neck formation.

Since the transition of a glassy polymer into the oriented state takes place precisely in the region of the neck, let us first consider fragmentation of the metallic coating in this region. Under uniaxial stretching of glassy PET, the zone of the forming neck is rather narrow. To expand this region and to study the beginning of the fracture process in the coating, we used the following technique. Films with a thin platinum coating were stretched by 15% at 90°C and then stretched again in the perpendicular direction at 20°C. In this case, the secondary drawing was accompanied by necking and the region of neck formation was fairly wide.

As is known, deformation of a glassy polymer is largely controlled by the initial content of defects. Evidently, disintegration of the coating into individual fragments at the first moment of neck formation will also proceed randomly (via the detachment mechanism) at stress concentration sites. However, both the width and the thickness of the sample in the region of the originating neck sharply decrease at the same time; this decrease corresponds to the natural draw ratio of polymer, and the true tensile stress in the region of the forming neck increases. If this stress exceeds the strength of the coating in the central part, further disintegration of the metal takes place and this process will develop until the cross section of the sample ceases to change and the tensile stress during further stretching becomes invariable.

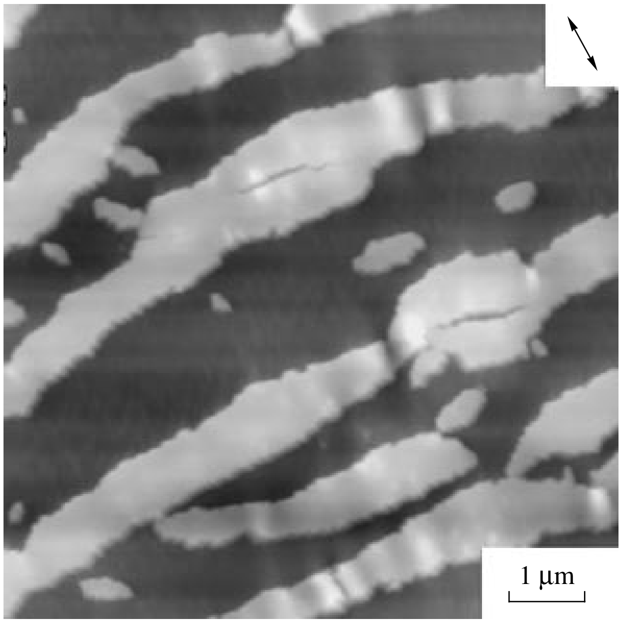

Fig. 2. AFM image of a surface fragment of a PET film with a thin (10.7 nm) platinum coating after stretching at 20°C with a strain rate of 0.2 mm/min.

Figure 3 presents the SEM image characterizing the surface structure of a PET sample with a deposited metallic coating after stretching by 15% at 90°C. As is seen, fracture of the coating at this low tensile strain proceeds randomly owing to activation of defects at stress concentration sites. As a result, the coating develops randomly distributed cracks, which are oriented perpendicular to the direction of stretching. Furthermore, even at low tensile strains of the polymer, stretching is accompanied by the formation of surface microtopography that is oriented along the direction of stretching. This pattern of fragmentation and topography formation in the coating was observed in [9–15].

Secondary stretching of a polymer sample with a deposited coating was performed at 20°C in the direction perpendicular to the direction of primary stretching, and a neck was formed as a result. Figure 3b shows the structure of the polymer surface in the region of necking. As is seen in the SEM image, where the central part characterizes the region of the forming neck, cracks in the coating formed during the first drawing are preserved but one can also observe further disintegration of the metal, and the direction of secondary cracks is perpendicular to the direction of primary cracks, which were formed during stretching at 90°C. As follows from this SEM image, nucleation of secondary cracks in the region of the forming neck is also random. In this case, the coating breaks down into fragments whose orientation is perpendicular to the direction of secondary stretching and whose length is limited by primary cracks. Such fragments are characterized by fairly nonuniform widths. However, one can clearly see

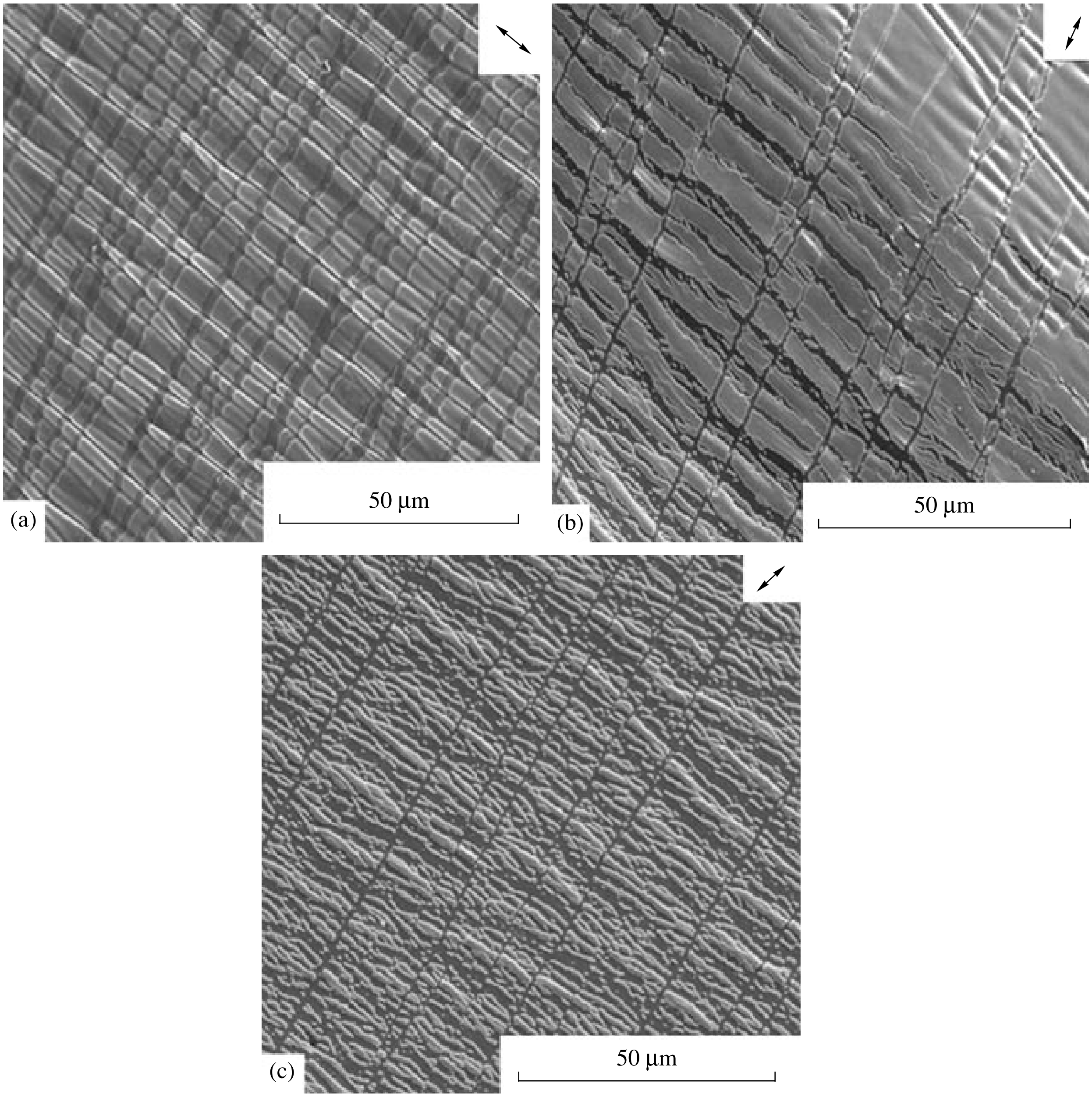

Fig. 3. SEM images of a PET film with a platinum coating with a thickness of 5.4 nm (a) after its uniform deformation by 15% at 90°C and (b, c) after its repeated stretching at 20°C in the direction perpendicular to the direction of primary stretching: regions of (b) neck nucleation and (c) the formed neck.

that, during necking, their dimensions tend to decrease further as the coating breaks down into numerous smaller fragments. Finally, in the region of the fully developed neck (Fig. 3c), the width of the metallic fragments is virtually uniform and their dimensions remain unchanged.

Note that earlier studies analyzing the mechanism of fracture of a thin rigid coating on a polymer substrate or in similar fiber-filled polymer systems usually consider the average dimensions of the fractured fragments. Analysis of the size distribution of these fragments allows the gain of far more complete information concerning fracture processes in the coating during deformation of the polymer substrate. Nevertheless, such analysis has been made in only a few publications [18, 19] and confirmed mainly for deformation of PET samples with a thin aluminum coating.

To unambiguously answer the question about the actual predominant mechanism of the coating fragmentation during tensile drawing of a glassy polymer that deforms via necking, statistical analysis of fragment widths was performed, the corresponding size distribution curves were plotted, and their relative variances were estimated.

As was shown earlier [18, 19], random fracture of a coating leads to a wide width distribution of the fragments with a relative variance close to unity. This mechanism of fracture is most probable at early stages of tensile drawing of PET at 90°C, when the polymer exists in the rubbery state. When fracture of fragments proceeds via their disintegration into two equal parts, the corresponding width distribution is narrow and the relative variance is ~0.2.

In this study, the width distribution of fragments of platinum or gold coatings deposited on a PET substrate is analyzed. Stretching was performed at room temperature, where PET exists in the glassy state. Figure 4 presents the typical size distribution curve of platinum fragments for a PET sample stretched at 20°C. The thickness of the deposited platinum layer was 5.4 nm. As is seen, the width distribution of the fragments is fairly narrow and shows a distinct maximum. The relative variance of this distribution is 0.35. Note that PET films with a thin deposited gold layer (14 nm) under the same stretching conditions are characterized by a similar fragment size distribution. The relative variance of this distribution is 0.27.

This observation implies that, during stretching of glassy PET, fragmentation of a rigid coating primarily proceeds via disintegration of each randomly formed fragment into two equal parts.

The fragment width distribution curves were plotted for glassy PET films with different thicknesses of the deposited platinum layer. Irrespective of the thickness and nature of the metallic layer (platinum or gold) on the surface of the polymer film, the width distribution of the fragments turned out to be similar for all samples under study and had a relative variance of 0.31–0.38.

It seems that processes in the narrow region between the unoriented polymer and the neck (which propagates along the sample during its deformation) have a mechanism that is similar to that observed during fragmentation of a polymer on a rubbery substrate. The transition region between the neck and the undeformed part of the polymer sample has a complex geometry. Within this region of a deforming polymer film, the thickness of the sample sharply decreases. As a result, the initially even film surface becomes sharply bent and the coating experiences cracking (detachment) with the formation of fairly long fragments with different widths. After the primary cracking, the polymer becomes stretched in this narrow transition region. Apparently, it is during this process that fragmentation of the coating via disintegration of primary fragments into two equal parts takes place. The resultant size distribution of the coating fragments is narrow, as is typical of this fragmentation mode.

So, plastic deformation of glassy PET with a rigid metallic coating is accompanied by fracture of the surface layer in the region of the forming neck. Nucleation of initial cracks is random; however, the predominant mechanism is disintegration of fragments into two equal parts and the final width of the fragments is controlled by this mechanism. In conclusion, note that a similar mechanism of coating fragmentation was also proposed for uniaxial stretching of PET at temperatures above its T_g. However, the width distribution of fragments formed during tensile drawing of glassy PET is narrower and has a smaller relative variance, thereby indicating a more marked influence of the mechanism of fragment disintegration into two equal parts.

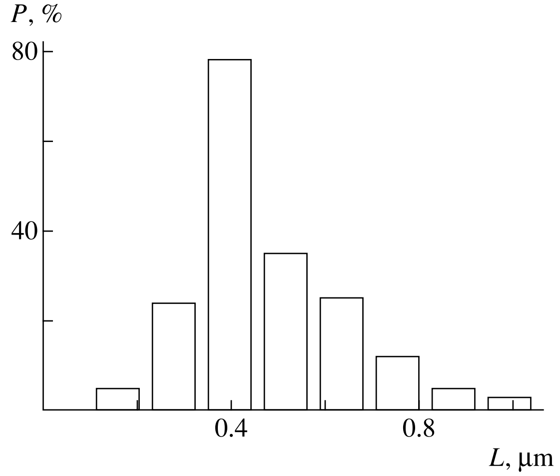

Fig. 4. Fragment width distribution curves for PET films with a platinum coating with a thickness of 5.4 nm after their stretching at 20°C at a strain rate of 0.2 mm/min. *P* is the probability of the appearance of fragments with given dimensions.

We express our sincere gratitude to S.L. Bazhenov for fruitful discussion and valuable comments.

REFERENCES

1. J. T. Felts, J. Plast. Film Sheeting **9**, 201 (1993).
2. D. R. Cairns, D. K. Sparacin, D. C. Paine, and G. P. Crawford, in *Proceedings of SID International Symposium*, San Jose, USA, 2000, p. 274.
3. *Metallized Plastics: Fundamental and Application*, Ed. by R. L. Mittal (Marcel Dekker, New York, 1998).
4. Y. Leterrier, L. Boogh, J. Andersons, and J.-A. E. Manson, J. Polym. Sci., Part B: Polym. Phys. **35**, 1449 (1997).
5. Y. Leterrier, J. Andersons, Y. Pitton, and J.-A. E. Manson, J. Polym. Sci., Part B: Polym. Phys. **35**, 1463 (1997).
6. Y. Leterrier and J.-A. E. Manson, in *Proceedings of European Conference on Macromolecular Physics, Morphology and Micromechanics*, Merseburg, Germany, 1998, p. 293.
7. C. S. Deng, H. E. Assender, F. Dinelli, et al., J. Polym. Sci., Part B: Polym. Phys. **38**, 3151 (2000).

8. V. Belyaev, L. Chistovskaya, V. Konovalov, et al., J. Soc. Inf. Display **11**, 3 (2003).
9. A. L. Volynskii, S. L. Bazhenov, and N. F. Bakeev, Ross. Khim. Zh. **42** (3), 57 (1998).
10. A. L. Volynskii, S. L. Bazhenov, O. V. Lebedeva, et al., J. Appl. Polym. Sci. **72**, 1267 (1999).
11. A. L. Volynskii, E. E. Voronina, O. V. Lebedeva, et al., Vysokomol. Soedin., Ser. A **42**, 262 (2000) [Polymer Science, Ser. A **42**, 177 (2000)].
12. S. L. Bazhenov, A. L. Volynskii, V. M. Alexandrov, and N. F. Bakeev, J. Polym. Sci., Part B: Polym. Phys. **40**, 10 (2002).
13. A. L. Volynskii, V. N. Nechaev, A. S. Kechek'yan, et al., Vysokomol. Soedin., Ser. B **43**, 2211 (2001) [Polymer Science, Ser. B **43**, 360 (2001)].
14. A. L. Volynskii, S. L. Bazhenov, O. V. Lebedeva, and N. F. Bakeev, J. Mater. Sci. **35**, 547 (2000).
15. A. L. Volynskii, O. V. Lebedeva, S. L. Bazhenov, and N. F. Bakeev, Vysokomol. Soedin., Ser. A **43**, 1488 (2001) [Polymer Science, Ser. A **43**, 921 (2001)].
16. E. E. Voronina, I. V. Yaminskii, A. L. Volynskii, and N. F. Bakeev, Dokl. Akad. Nauk **365**, 206 (1999).
17. L. M. Yarysheva, D. A. Panchuk, A. V. Bol'shakova, et al., Vysokomol. Soedin., Ser. A **47**, 1652 (2005) [Polymer Science, Ser. A **47**, 968 (2005)].
18. Khe Tsyanpin, Candidate's Dissertation in Chemistry (MGU, Moscow, 2000).
19. A. L. Volynskii, Khe Tsyanpin, S. L. Bazhenov, et al., Vysokomol. Soedin., Ser. A **47**, 747 (2005) [Polymer Science, Ser. A **47**, 436 (2005)].